The Electronic Studies of Lead Bromide, Bismuth Bromide and Indium Chloride Molecules.

KRISHNA MURARI LAL,
M. Sc., (Benaras)

Thesis submitted in the Partial Fulfilment of the Requirements for the award of the Degree of Doctor of Philosophy of
ALIGARH MUSLIM UNIVERSITY
ALIGARH, INDIA.
1968

Certified that the work presented in this thesis is the original work of Mr. Krishna Murari Lal, done under my supervision.

10.10.'68

(DAIJ NATH KHANNA)

Department of Physics,
Aligarh Muslim University,
Aligarh (U.P.)
INDIA.

PREFACE

The thesis deals with the rotational spectra of lead monobromide, bismuth monobromide and indium monochloride molecules and is divided into three chapters. The spectra of these halides have been obtained mostly with a 2450 Mc/s microwave oscillator as well as with an eight kilowatt transformer.

Chapter I deals with the emission spectrum of the visible band system of lead monobromide molecule. The spectrum has been recorded with the help of the microwave oscillator and nearly 110 red degraded bands were measured as against 52 bands obtained by Morgan in absorption. The rotational structure of the (3, 2), (2, 2), (4, 2) and (4, 1) bands of this system has been photographed in the second order of a 35 ft concave grating spectrograph. The structure due to bromine isotopes has been resolved and the rotational constants for the $Pb^{79}Br$ and $Pb^{81}Br$ molecules have been determined. The study of the rotational structure alongwith a detailed discussion of the electronic configuration enabled the determination of the probable electronic transition.

Chapter II deals with the emission spectrum of the

visible band system of bismuth monobromide molecule. The structure of the (7, 0), (8, 0), (9, 0), (10, 1), (0, 6), (0, 7) and (1, 4) bands excited with the help of the microwave oscillator has been recorded in the second order of a 35 ft concave grating spectrograph. The rotational constants for the two isotopic molecules $Bi^{79}Br$ and $Bi^{81}Br$ have been obtained. A study of the rotational structure reveals that the coupling is of Hund's case (c) type, therefore the electronic transition has been concluded to be $^3\Pi(0^+) - {}^3\Sigma^-(0^+)$.

Chapter III deals with the emission spectrum of indium monochloride molecule, excited with the help of the microwave oscillator. The rotational structure of the (0, 0), (0, 1) and (1, 0) bands of the B-X system has been photographed in the second order of a 35 ft concave grating spectrograph. The rotational lines for the $In^{115}Cl^{35}$ molecule have been identified and the constants have been determined. The ground state internuclear distance has been found to be the same as that observed by Youngner and Vinans from the rotational analysis of the A-X system in absorption. A detailed discussion of the electronic transition involved in the system has been given.

The different chapters in this thesis are written

in a form suitable for publication. Each chapter contains a separate introduction and a separate abstract. A general introduction is therefore not given.

All the work described in this thesis has been initiated, prosecuted and completed under the inspiring guidance of Dr.B.N.Khanna; Physics Department, Aligarh Muslim University, Aligarh; to whom my grateful thanks are due. I am grateful to Professor Rais Ahmed, Head of the Department of Physics, Aligarh Muslim University, Aligarh for his continued interest and encouragement in the progress of the work. I am sincerely thankful to the Council of Scientific and Industrial Research, India, for the award of a Senior Fellowship in a Research Scheme sanctioned to Dr.B.N.Khanna.

I take this opportunity to express my deep sense of gratitude to Professor Nand Lal Singh, for the kind permission and help to record the spectra on 35 ft concave grating spectrograph, at the Department of Spectroscopy, B.H.U., Varanasi. Thanks are also due to my all teachers and colleagues at Varanasi for varied kind of help and encouragement rendered to me.

I wish to express my thanks to all the colleagues

and friends at the Department of Physics, A.M.U., Aligarh especially to Dr.P.K.Verma, Messrs Y.Kumar, R.K.Misra, Z.H.Zaidi and Mr.Laxmi Narain for their help and encouragement. Finally, I wish to thank Mr.M.H.Naqvi for the efficient typing of the manuscript.

Krishna Murari Lal

Krishna Murari Lal

C O N T E N T S

CHAPTER X

Emission Spectrum of the PbCl Molecule.

ABSTRACT

The emission spectrum of the visible band system of the PbBr molecule in the region 4600 Å – 6100 Å has been obtained. About 110 bands have been observed in the present experiment of which only 52 were recorded by earlier workers. The vibrational constants obtained are the same as those obtained by Morgan from absorption experiments.

The rotational structure of some of the bands of this system has been recorded in the second order of a 35 ft concave grating spectrograph at a dispersion of 0.32 Å/mm and the analysis of four bands (3, 2), (2, 2), (4, 2) and (4, 1) has been done. In all, four branches have been observed for each of the bands and they have been explained as the P and R branches due to $Pb^{79}Br$ and $Pb^{81}Br$. The molecular constants obtained are:

		$Pb^{79}Br$	$Pb^{81}Br$
D_e'	cm^{-1}	0.0065	0.0070
D_e''	cm^{-1}	0.0455	0.0466
r_e'	Å	2.76_0	2.76_6
r_e''	Å	2.54_6	2.54_5

$\alpha_e' = 0.00015\ cm^{-1}$; $\alpha_e'' = 0.00015\ cm^{-1}$

A detailed consideration of the electronic configuration and the probable states involved is given. The experimental observation, that only P and R branches occur in the rotational structure, indicates that the coupling in the molecule is probably of the Hund's case (c) type and the electronic transition involved in the emission of the system is probably $\frac{1}{2} - \frac{1}{2}$, similar to the A–X system of the PbCl molecule in the visible region.

INTRODUCTION

Spectroscopic studies of lead halides had been undertaken for the first time by Barratt[1] who recorded the absorption spectrum of the PbCl molecule but gave no analysis of the bands. Howell and Rochester[2] obtained the visible band systems of the PbBr and PbF molecules in a high frequency electrical discharge but he too failed to give any of the molecular constants. Morgan[3] for the first time made a detailed investigation of the visible band systems of the PbF, PbCl and PbBr molecules in absorption, through an open graphite tube placed in a furnace and obtained their vibrational constants. The analyses are supported by the isotopic shifts of the bands due to halogen isotopes. Rochester[4] again took up the studies and obtained six systems for the PbF molecule. He established the doublet nature of the ground state in PbF for which the doublet separation was found to be 0266 cm^{-1}. Wieland and Newburgh[5] obtained another system D - X in absorption in the ultraviolet region in each of the halides PbCl, PbBr and PbI.

Thus the only satisfactory experimental data about the visible band system of the PbBr molecule is that given by Morgan[3] who recorded 52 red degraded bands in absorption

in the region 4500 Å - 5300 Å and made a vibrational analysis. The following formula for $Pb^{79}Br$ bands was given:

$$Pb^{79}Br, \quad \nu = 20034.3 + (152.5u' - 0.40u'^2 + 0.020u'^3) - (207.5u'' - 0.50u''^2)$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

It was therefore considered worthwhile to develop the emission spectrum of PbBr in a closed discharge tube. Different sources of excitation were tried and it was found that the visible system is excited strongly with the microwave oscillator giving rise to a large number of new bands upto 6000 Å region. Inspite of serious efforts, the B-X system did not appear at all in emission. The first part of this chapter deals with the vibrational analysis of the extended system in emission.

As no rotational structure of this band system was observed and analysed so far, we planned to record the bands at a high resolution to obtain the rotational constants. The difficulty which one faces in resolving the rotational structure of the lead monobromide molecule is the presence of different isotopes of lead and bromine. Lead has got three isotopes with appreciable natural

abundance as follows:

^{206}Pb = 26.26 %

^{207}Pb = 20.32 %

and ^{208}Pb = 51.55 %

i.e. in the ratio of 1:1:2. Bromine has got two isotopes ^{79}Br and ^{81}Br of almost equal abundance. A most favourable situation will lead us to believe that out of the different isotopes of lead, only ^{208}Pb will contribute appreciably in the spectrum of lead monobromide molecule, while the other isotopes of lead will be washed off at higher rotational quantum numbers. This will simplify our analysis as we have only two isotopes of bromine of equal abundance.

The rotational structure of the visible band system of other halides of lead had been studied extensively and a common pattern had been observed. Rao, K.M. and Rao[6] reported the rotational analysis of the A-X system of the PbF molecule and the same year Rao, V.S. and Rao[7] gave the rotational analysis of the A-X system of PbCl. In case of both these molecules only one P and one R branch has been observed. On this ground it was suggested that the systems arise from a $^2\Sigma \rightarrow {}^2\Sigma$ transition. If we take

the analogy of the other halides of lead, we expect only two branches for a single isotopic specie in PbBr molecule. To a first approximation if we take only ^{208}Pb (50.57 %) into consideration, whose abundance is twice that of the other two species of lead, we expect to observe bands due to $^{208}Pb^{79}Br$ and $^{208}Pb^{81}Br$ molecules of equal abundance. These two will give rise to a four branch structure for a band on the basis of facts mentioned earlier. This expectation is further supported by the following observation:

The double-headed character of the bands is maintained even in the second order of 35 ft grating spectrogram and no other heads are observed. This indicated that the contribution due to the other lead isotopes is very weak as compared to bromine isotopes because of which almost all the bands show two heads of equal intensity.

Morgan[3] has given the vibrational analysis of the bands of PbBr from a spectrogram taken in the second order of a 10 ft concave grating spectrograph having a dispersion of 3.72 Å/mm and could not observe any rotational structure. At first, the spectrum was recorded in the second order of a 21 ft concave grating spectrograph in the region (4650 Å - 4050 Å) where the bands namely

(3, 2), (2, 2), (3, 1) and (4, 1) are free from any serious overlapping and show a rotational structure consisting of two series of lines Fig.3. An analysis of these four bands was carried out and results were published. We observed a broadening in both the branches for all the bands at higher J values and mentioned that the broad lines may show isotopic splitting at a higher resolution. Later the emission spectrum has been recorded in the second order of a 35 ft concave grating spectrograph at a dispersion of 0.32 Å/mm at the Department of Spectroscopy, B.H.U., Varanasi. The grating has 30,000 lines per inch with a ruled width of 6 inches and blazed at 7500 Å in the first order. The structure of the (3, 2) band Fig.4 reveals that the above mentioned broad lines of Fig.3 at higher J are a group of four lines, which have been explained as the two P and two R branches due to $Pb^{79}Br$ and $Pb^{81}Br$ isotopic heads of equal intensity. The rotational analysis of four bands (3, 2), (2, 2), (4, 2) and (4, 1) bands are given in this chapter. The isotopic branches are given separately for two bands (3, 2) and (2, 2) as only the structure of these two bands allows to sort out the four branches conveniently. The electronic transition involved in the system is also discussed.

EXPERIMENTAL DETAILS

The spectrum was obtained in emission exciting the pure sample of $PbBr_2$ (B.D.H.) with a 2450 Mc/sec microwave generator in an U shaped pyrex tube 5 cm in diameter closed at one end and held vertically. The open limb was connected to a rotary pump and was continuously pumped. The antenna of the microwave generator was placed at the mid point of the closed limb, 2 cm in length, and the substance was kept at the curved portion of the U tube. Only a small amount of the substance was kept inside the tube so that it might not block the bent portion of the U tube after melting down. Heat generated by the microwave oscillator was sufficient to evolve requisite amount of vapour and so no external heating was found necessary. This arrangement gave a brilliant greenish discharge which was a better emitter of the bands under consideration as compared to high frequency or transformer discharge. The visible bands were recorded first on a three prism glass spectrograph and then in the first and second orders of a 21 ft concave grating spectrograph (Eagle mounting) having 15,000 lines per inch at a dispersion of 1.25 Å/mm in the second order. Some of the bands were also photographed in the second order of a 35 ft concave grating

spectrograph at a dispersion of 0.32 Å/mm. The grating was blazed at 7500 Å in the first order.

Exposure time required to record the bands on the three prism glass spectrograph ranged from 10 to 20 minutes, whereas the time needed in the second order of 21 ft grating spectrograph was 2 to 3 hours. Ilford HP3 and GEVO Blau Rapid plates were used to photograph the bands. Nearly 6 to 8 hours exposure time was needed for recording some of the strong bands in the second order of 35 ft grating spectrograph on GEVO Blau Rapid plates. Iron arc spectrum run at low current in air was superimposed as standard for the measurement of plates, done with the help of a Carl Zeiss Abbe comparator. Wavelength of standard lines have been taken from M.I.T.Wavelength Tables (Harrison[9]) and converted to wave-numbers in vacuo from the Table of Wavenumbers (N.B.S.[9]). The accuracy of our measurements is of the order of $\pm$ 0.04 cm^{-1} for sharp lines and $\pm$ 0.10 cm^{-1} for broad diffuse lines.

VIBRATIONAL ANALYSIS

The bands of the A-X system of the lead monobromide molecule lie in the region 4600 Å - 6000 Å and are red degraded. An enlarged reproduction of the spectrum taken

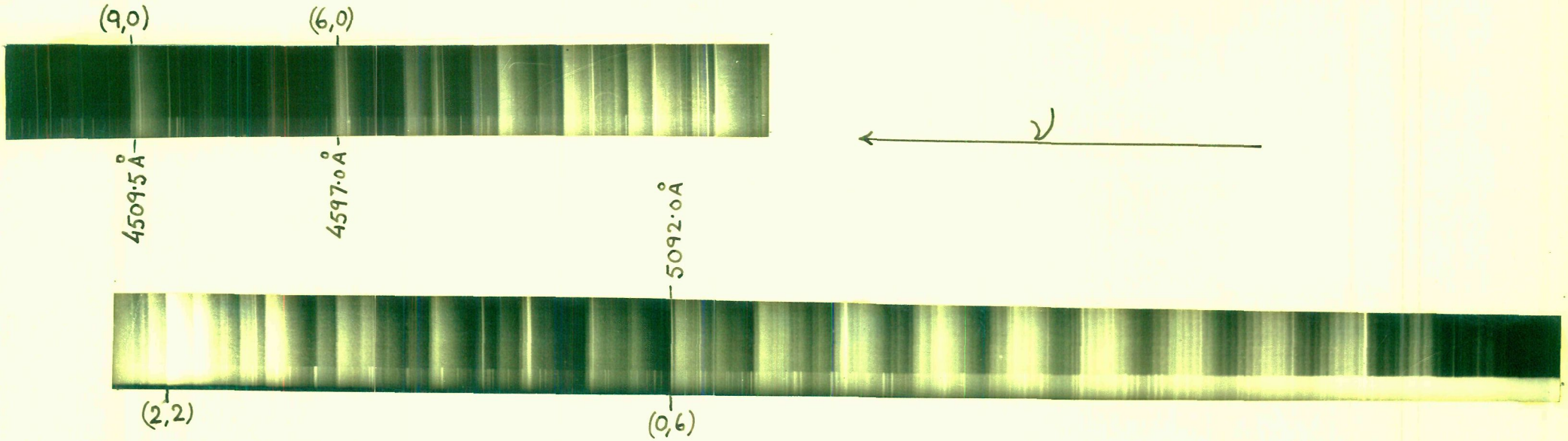

Fig. 1. The Enlargement of the 4500 - 6000 Å System of the PbBr (Three - prism glass spectrograph)

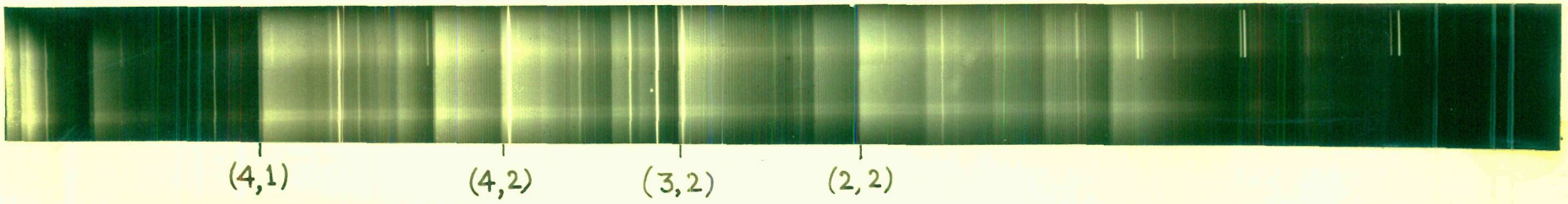

Fig. 2. The Contact - print of the bands (4650 - 4850 Å) obtained in the second order of a 21 ft grating spectrograph.

on three prism glass spectrograph is shown in Fig.1 and the contact print of the spectrogram taken in the second order of 21 ft grating spectrograph is given in Fig.2. All the bands show two heads of equal intensity suggesting that they arise from ^{79}Br and ^{81}Br isotopes. The isotopic separation of the bands confirms the vibrational analysis given by Morgan[3]. In all about 110 bands were measured and their vibrational assignments made on the basis of observed isotopic shifts with the result that almost all the bands fit in the same system (Morgan). The Condon parabola is very wide, indicating that a large difference exists between the internuclear distances of the two electronic states involved. Wavelengths, wavenumbers and the visually estimated relative intensities of the bands are given in Table I. The bands observed in absorption by Morgan are also included in the table for comparison.

The agreement between the isotopic shifts obtained from the present experiment and those observed by Morgan in absorption indicates clearly that this band system can most probably be attributed to Br_2 molecule. All the bands fit into the formula given by Morgan without any difficulty and therefore the vibrational constants did not require any change (Lal and Khanna[10]).

TABLE I:- Band head data of the A-X System of the PbBr molecule.

v'	v"	I	$\nu(Pb^{79}Br)$ Present Investigation	$\nu(Pb^{79}Br)$ Morgan.	$\nu(Pb^{79}Br) - \nu(Pb^{81}Br)$ Calc.	Obs. Present	Obs. Morgan
14	2	2	22413.1	-	-	-	-
10	0	4	22303.0	22303.4	-	-	-
9	0	4	22169.3	22169.1	10.5	10.3	10.8
8	0	4	22001.9	22002.2	9.6	10.0	10.3
7	0	5	21091.1	21090.4	0.5	0.5	0.1
9	2	6	21759.4	-	-	7.1	-
6	0	7	47.3	21746.0	7.4	7.1	6.6
7	1	5	21685.6	21685.9	6.6	7.4	7.7
8	2	3	10.5	20.2	5.0	4.6	5.2
5	0	6	02.7	03.1	6.2	6.9	6.0
6	1	5	21541.9	21540.9	5.5	5.6	5.2
7	2	3	21481.2	21475.4	-	-	-
4	0	0	56.4	55.5	5.1	4.9	6.2
8	3	3	16.0	-	-	3.2	-
5	1	0	01356.0	21396.4	4.3	4.0	4.7
9	4	2	52.9	-	-	-	-
3	0	4	06.9	09.1	3.8	3.5	4.3
7	3	3	21276.0	21275.1	2.9	2.6	3.1
4	1	9	50.4	49.4	3.2	3.2	3.2
5	2	1	21190.0	21190.3	-	-	-
2	0	2	57.7	-	-	-	-

TABLE I (Continued)

v'	v''	I	Present	Morgan	Calc.	Fre-mont	Morgan
9	5	1	21143.2	-			
6	3	4	32.4	21132.2			
3	1	7	02.5	01.2	2.5	2.0	1.9
4	2	10	21044.4	21044.5			
1	0	1	11.2	11.6			
5	3	2	20987.7	20987.6			
2	1	9	92.7	91.5			
6	4	5	30.0	29.0			
3	2	10	20090.2	20096.5			
1	1	3	02.0	01.5			
5	4	5	20704.4	20704.1			
2	2	10	47.6	47.6	-1.4	-1.4	-1.4
3	3	6	20692.9	20692.8	-	-1.2	-
4	4	4	37.6	38.6			
1	2	5	20697.2	20697.7			
2	3	8	43.2	43.4	-3.2	-3.0	-3.2
4	5	7	20433.7	20432.4			
1	3	6	20302.0	20301.8	-4.5	-4.3	-4.4
2	4	4	39.2	39.0	-5.0	-4.8	-5.2
6	7	3	15.5	-			
3	5	5	20204.3	20206.9	-5.4	-4.6	-4.4
0	3	4	40.1	40.4	-5.9	-5.3	-5.7

TABLE X (Continued)

v^1	v^3	I	Present	Morgan	Calc.	Ino-sent	Morgan
1	4	8	20100.4	20100.2	-6.3	-6.2	-6.3
5	7	3	77.2				
3	6	5	20004.4	20004.8	-7.2	-6.8	-6.9
0	4	5	20006.3	06.8	-7.7	-7.9	-7.3
1	5	6	19986.3	19986.3	-8.1	-8.3	-7.8
2	6	3	34.3	33.4	-8.6	-	-8.7
3	7	3	19933.8			-8.5	
0	5	6	33.5	19934.3	-9.5	-10.2	-8.9
4	8	4	25.0				
1	6	2	19734.0	19733.2	-9.9	-10.0	-8.9
2	7	3	34.3	33.7	-10.4	-9.4	-10.7
0	6	6	19602.8	19602.9	-11.3	-10.0	-10.9
1	7	2	19303.0			-10.0	
2	8	5	34.2	19503.6	-12.1	-12.2	-11.1
3	9	3	19403.6			-12.4	
0	7	6	32.0	19432.7	-13.2	-12.0	-12.3
1	8	4	19304.8	19302.8	-13.4	-	-12.7
2	9	3	35.2				
3	10	3	19207.4		-13.9	-14.4	
0	8	6	33.0	19233.5	-14.0	-13.7	-13.2
1	9	3	19134.6			-14.8	
2	10	3	40.0				

TABLE I (Continued)

v'	v''	I	Present	Morgan	Calc.	Present	Morgan
3 ,	11	4	19090.7		-15.6	-14.5	
0 ,	9	6	30.4	19034.9	-16.5	-16.3	-15.6
1 ,	10	4	19987.8	18983.6	-16.8	-16.6	-14.9
2 ,	11	2	30.3				
3 ,	12	2	10095.5		-17.2	-16.0	
4 ,	13	2	92.0				
0 ,	10	5	36.5		-17.9	-17.0	
1 ,	11	5	10791.2	13790.9	-18.5	-18.0	-17.8
6 ,	15	4	60.3				
2 ,	12	4	44.5				
1 ,	12	5	10599.0		-19.9	-20.1	
2 ,	13	4	48.7		-20.2	-20.7	
3 ,	14	4	06.6				
4 ,	15	4	10462.5				
0 ,	12	4	40.1		-21.2	-20.4	
1 ,	13	4	10390.5		-21.6	-22.6	
2 ,	14	5	55.6		-21.8	-22.0	
3 ,	15	5	11.6		-22.2	-22.0	
4 ,	16	5	10266.9		-22.4	-22.1	
1 ,	14	4	04.5		-23.1	-21.8	
6 ,	17	4	10105.1				
2 ,	15	4	55.4				

TABLE I (Continued)

v'	v''	I	Present	Morgan	Calc.	Present	Morgan
3	16	5	18110.3		-23.7	-24.3	
4	17	5	18073.6		-23.9	-23.6	
0	14	5	58.1				
5	18	5	30.2		-24.2	-24.9	
6	19	6	17994.1				
2	16	5	60.0		-25.1	-25.3	
7	20	4	53.0				
3	17	4	26.2		-25.3	-26.8	
4	18	5	17883.2		-25.5	-26.5	
0	15	3	67.1				
5	19	4	40.6		-25.7	-26.5	
3	18	3	17734.2		-26.0	-26.1	
4	19	2	17693.2		-27.1	-28.9	
5	20	2	51.0		-27.3	-28.0	
6	21	2	08.1		-27.5	-29.5	
3	19	2	17543.1				
5	21	2	17462.8		-28.7	-28.4	
6	22	2	19.0		-29.0	-30.5	
6	20	2	17233.3				

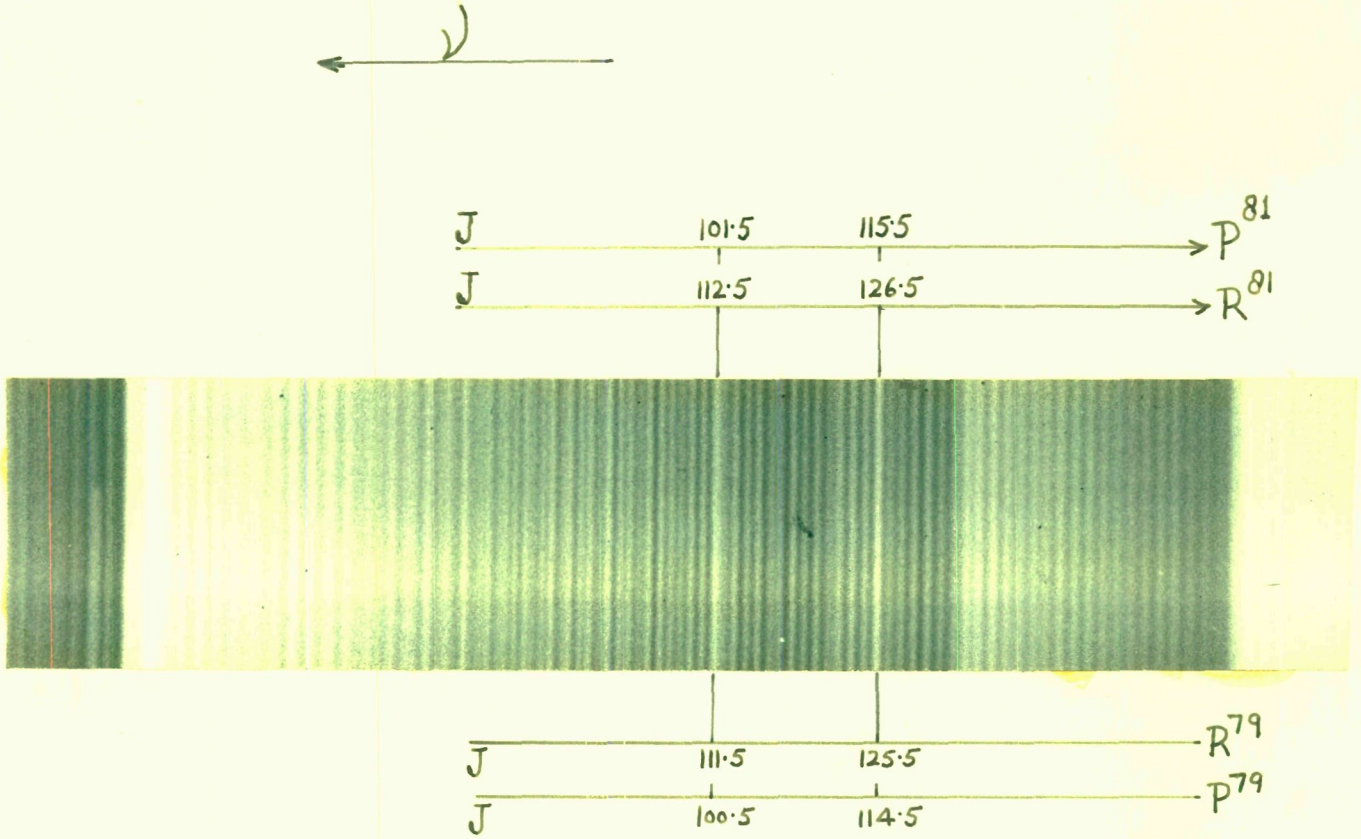

Fig. 3. The Enlargement of the (3, 2) band of the (4500 -6000 Å) System of PbBr (21 ft grating II order)

ROTATIONAL ANALYSIS

The enlarged spectrum of the (3, 2) band photographed in the second order of the 21 ft grating spectrograph is shown in Fig.3. A careful observation of the plate shows the presence of two series of lines. An analysis of the (3, 2), (2, 2), (3, 1) and (4, 1) bands from the record taken in the second order of the 21 ft grating spectrograph was made and the results were published by Lal and Khanna[10]. A broadening in the rotational lines was observed for all the bands at large J values and it was mentioned in the paper that at high resolutions these broad lines may show isotopic splitting.

In order to resolve the aforesaid isotopic splitting if any, the (3, 2), (2, 2), (4, 2) and (4, 1) bands were later on recorded in the second order of a 35 ft concave grating spectrograph having a theoretical resolution of 3,60,000. The enlargement of the spectrograms of the bands are given in Figs.4, 5 and 6.

On looking at the structure of the (3, 2) band (Fig.4), one finds that the lines at large J values which appear as broad ones on the 21 ft grating spectrogram, (Fig.3), are a group of four lines. To start the rotational analysis we took first the (3, 2) band for which the vibrational

isotopic shift is + 0.03 cm^{-1}. The rotational structure of this band appears to be simple and free from any overlapping. Near the band head (Fig.4 A, B) there is a single series of lines. Naturally one takes that this series of lines represents the P and R branches of both the species of molecule overlapped. With the help of these lines, combination differences and there from an approximate B values for the (3, 2) band were found out. It has been observed from the previous analysis given by Lal and Khanna[10], that the band origin is very near to the band head. All the four branches ^{79}P, ^{79}R, ^{81}P and ^{81}R, which were expected to appear in the structure of the bands, as discussed in the introduction, were calculated using the above mentioned approximate B values and the band head as band origin, from the formula (Herzberg[11], page 174):

$$\nu = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v - D'_v + D''_v)m^2 - 2(D'_v + D''_v)m^3 - (D'_v - D''_v)m^4 \quad \ldots\ldots(1)$$

where m = -J for P branch and (J + 1) for R branch. The approximate calculated value of D''_0 from the relation:

$$D_0 = \frac{4B_0^3}{\omega_0^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

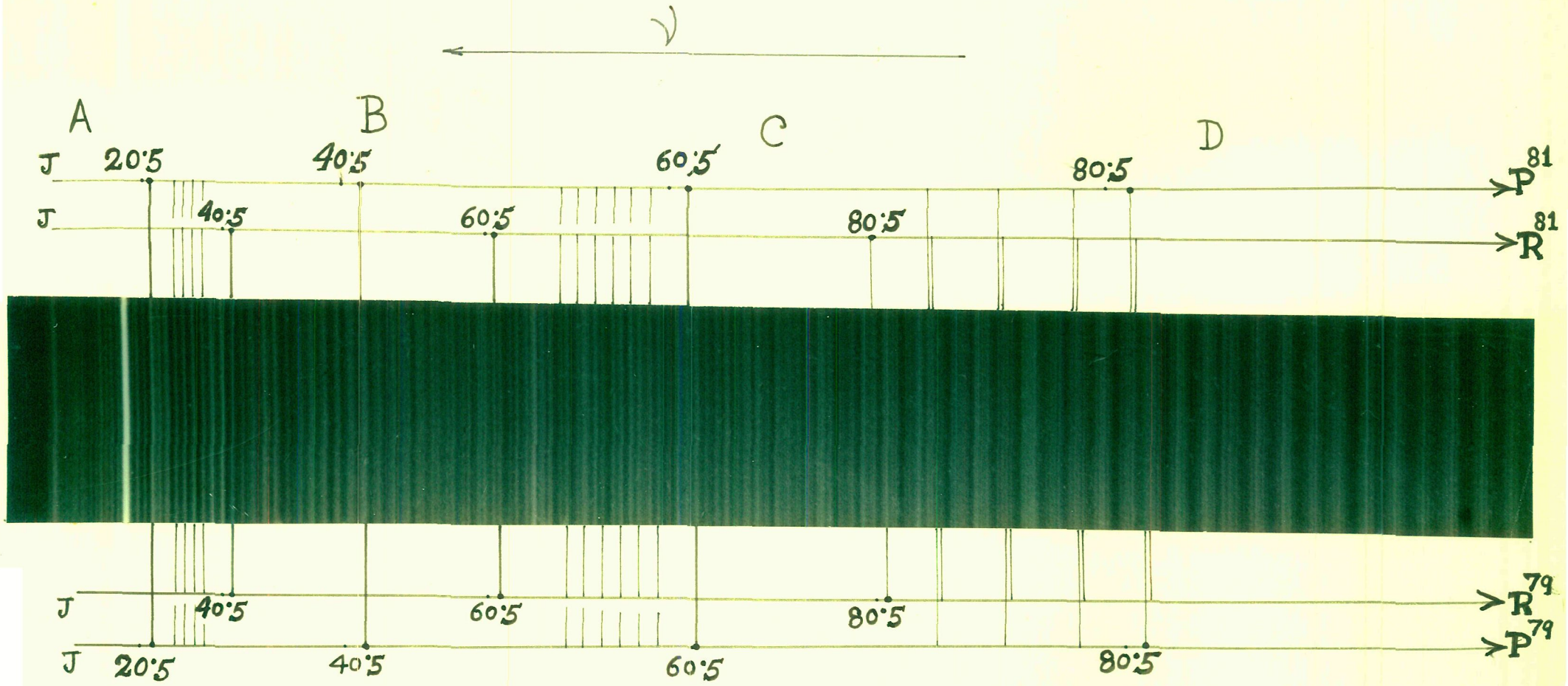

Fig. 4. The Enlargement of the (3, 2) band of the (4500 - 6000 Å) System of PbBr (35 ft grating II order).

is 1×10^{-3} cm^{-1}, which is very small as compared to D_o (D_o (approx) $= 4 \times 10^{-2}$ cm^{-1}) therefore its contribution to the m^2 term is negligible. At large m values the terms containing third and fourth powers of m are significant and have been taken care of in the calculation. It was found that the measured values of the four series of lines appearing in the portion (C, D Fig.4) of the (3, 2) band tally very closely with the calculated four branches — each pair belonging to one isotopic band head. Thus we arrived at the conclusion that in the beginning the four branches are overlapped giving a single series structure; later at medium J values (D, C Fig.4) this single series splits into two series of lines, each one belonging to one isotopic head — the P and R branches still unresolved. At large J values (C, D Fig.4) each of the two series further splits into two lines resulting into a four line structure and the P and R branches get resolved for both the isotopes. As the R branch is the returning branch — out of the two lines which got separated at large J values the farther one from the band head has been taken as the R branch line.

All the four branches have been sorted out for two bands (3, 2) and (2, 2). The structure of the other two bands (4, 2) and (4, 1) does not permit to sort out all

these branches due to overlapping of (2, 1) and (3, 1) bands respectively. The wavenumbers of the two branches belonging to $Pb^{79}Br$ head of (3, 2), (2, 2), (4, 2) and (4, 1) bands are given in Table II. The wavenumbers of the rotational lines belonging to $Pb^{81}Br$ head of the (3, 2) and (2, 2) bands are given in Table III.

The rotational analysis in case of a band containing two branches is simple. To every line in the P branch there is a corresponding line in the R branch having the same upper rotational level. The wavenumber difference of these two lines, $\Delta_2 F''(J)$, is equal to the separation of one of the lower state rotational levels from the next but one.

$$R(J-1) - P(J+1) = F_v''(J+1) - F_v''(J-1) = \Delta_2 F_v''(J) \quad \ldots(3)$$

Similarly, the separation of one of the upper state rotational levels from the next but one is equal to the difference between wavenumbers of the R and P lines with a common lower state.

$$R(J) - P(J) = F_v'(J+1) - F_v'(J-1) = \Delta_2 F_v'(J) \quad \ldots\ldots(4)$$

The position of the rotational levels can be obtained after we find out the combination differences $\Delta_2 F''(J)$ and $\Delta_2 F'(J)$ values. Substituting the value of the

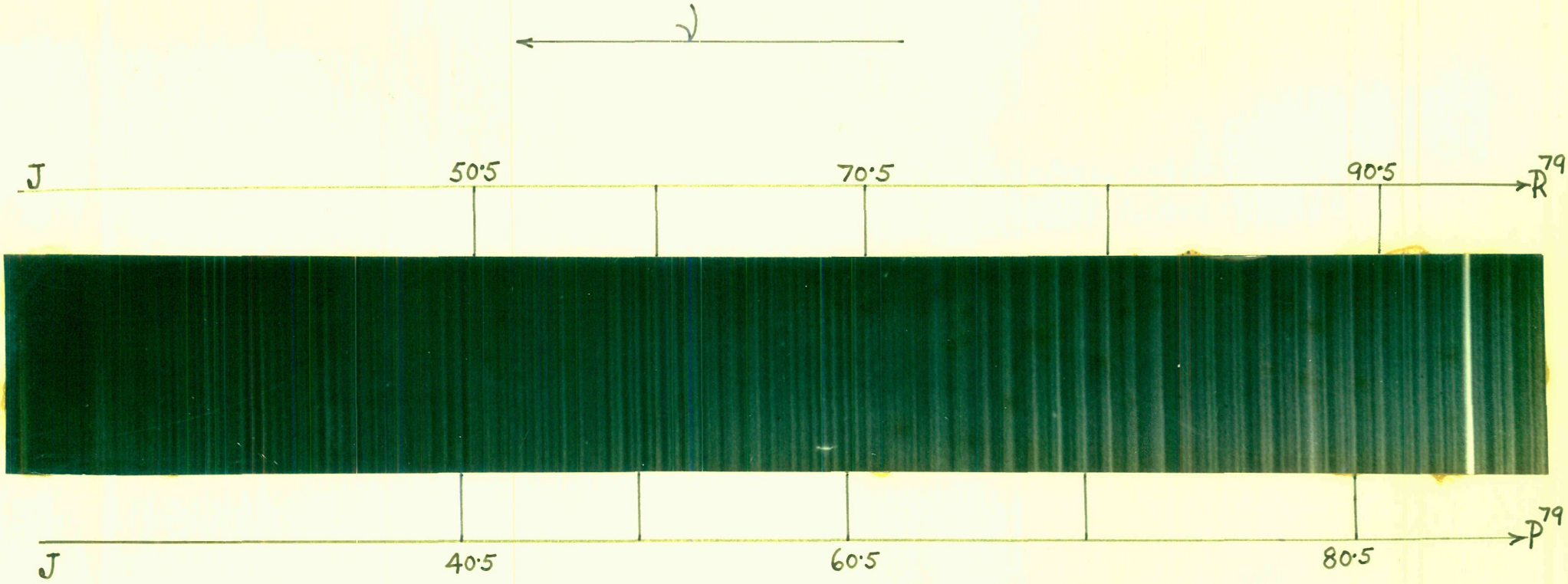

Fig. 6. The Enla-rgement of the (4, 1) band of the (4500 -6000) System of PbBr (35 ft grating II order).

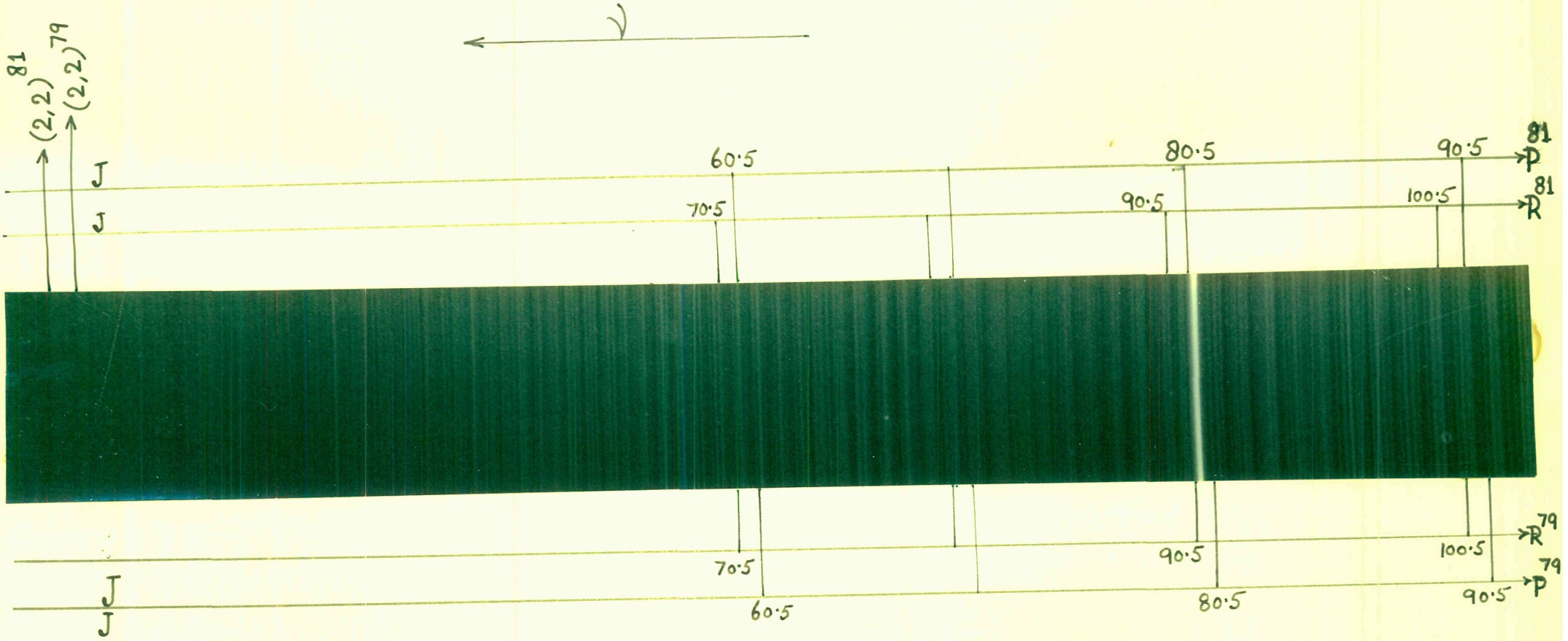

Fig. 5. The Enlargement of the (2, 2) band of the (4500-6000 Å) System of PbBr (35 ft grating II order).

TABLE II. Vacuum Wavenumbers and Rotational Assignments for (3, 2), (2, 2), (4, 2) and (4, 1) bands of $_{37}Rb^{79}Br$ molecule.

J	3 – 2		2 – 2		4 – 2		4 – 3	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
9.5		20393.63						
10.5		93.41						
11.5		93.15						
12.5		92.88						
13.5		92.70						
14.5		92.36						
15.5		92.05						
16.5		91.79						
17.5		91.44						
18.5		91.14						
19.5		90.74						
20.5	20393.88	90.40						
21.5	93.41	90.05						
22.5	93.15	89.65						
23.5	92.80	89.26	—	20740.31	—	—	—	—
24.5	92.47	88.87	—	39.08	—	—	—	—

TABLE II (continued)

J	3 - 2		2 - 2		4 - 2		4 - 1	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
25.5	[illegible]	[illegible]		20739.45				
26.5	92.25	88.78		39.02				
27.5	91.79	87.47		38.55				
28.5	91.44	87.38		37.99				
29.5	91.14	86.56		37.34				
30.5	90.74	86.07		36.79				
31.5	90.40	85.51		36.27				
32.5	90.05	85.08		35.71				
33.5	89.69	84.46		35.22		21026.90		21232.06
34.5	89.26	83.89	20740.31	34.38		26.29		32.16
35.5	88.87	83.37	39.88	34.33		25.55		31.46
36.5	88.43	82.76	39.45	33.73		24.90		30.77
37.5	88.00	82.15	39.02	33.09		24.15		30.11
38.5	87.47	81.41	38.55	32.44		23.38		29.39
39.5	87.08	80.84	37.99	31.67		22.68		28.61
40.5	86.55	80.19	37.34	31.02		21.93		27.85
41.5	86.07	79.48	36.79	30.29	—	21.27	—	27.13
42.5	85.51	78.88	36.27	29.73	—	20.77	21232.06	26.38

TABLE II (continued)

J	R(J) 3 - 2	P(J) 3 - 2	R(J) 2 - 2	P(J) 2 - 2	R(J) 4 - 2	P(J) 4 - 2	R(J) 4 - 1	P(J) 4 - 1
43.5	20035.03	20077.14	20735.71	20720.92	21026.50	21020.10	21230.15	21225.36
44.5	34.46	77.44	35.15	20.27	26.20	19.32	31.46	24.56
45.5	33.39	76.74	34.61	27.54	25.55	18.51	30.77	23.73
46.5	33.37	76.00	34.03	26.73	24.90	17.70	30.11	22.88
47.5	32.76	75.26	33.43	25.91	24.15	16.88	29.39	22.09
48.5	32.15	74.52	32.74	25.10	23.39	16.00	28.61	21.18
49.5	31.41	73.73	32.10	24.41	22.60	15.11	27.85	20.28
50.5	30.34	72.95	31.45	23.68	21.90	14.27	27.13	19.32
51.5	30.19	72.21	30.31	22.77	21.27	13.43	26.33	18.33
52.5	29.49	71.30	30.16	21.96	20.54	12.51	25.51	17.43
53.5	28.50	70.60	29.43	21.14	19.70	11.59	24.70	16.45
54.5	28.14	69.72	28.75	20.28	18.95	10.66	23.84	15.41
55.5	27.44	68.85	28.06	19.42	18.11	09.65	23.02	14.46
56.5	26.74	68.03	27.24	18.56	17.27	08.66	22.27	13.52
57.5	26.00	67.11	26.47	17.65	16.52	07.73	21.29	12.47
58.5	25.26	66.24	25.69	16.66	15.51	06.81	20.32	11.50
59.5	24.52	65.37	24.96	15.76	14.67	05.79	19.52	10.49
60.5	23.73	64.41	24.15	14.86	13.96	04.73	18.72	09.40
61.5	22.93	63.50	23.37	13.91	13.12	03.72	17.87	08.37

TABLE II (continued)

J	3 - 2		2 - 2		4 - 2		4 - 1	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
62.5	20373.21	20362.50	20722.56	20712.93	21012.15	21002.66	21216.92	21207.23
63.5	71.33	61.53	21.74	12.03	11.13	01.63	15.93	06.12
64.5	72.62	60.62	20.93	11.04	10.20	00.41	14.99	05.09
65.5	69.72	58.53	20.07	10.05	09.32	20999.39	13.99	03.07
66.5	68.85	57.62	19.21	09.03	08.44	98.29	12.96	02.75
67.5	68.33	57.53	19.31	08.04	07.47	97.19	11.92	01.53
68.5	67.11	56.62	17.43	06.92	06.45	96.39	10.89	00.30
69.5	66.26	55.53	17.43	06.01	06.39	94.93	09.83	21199.28
70.5	65.37	54.53	16.57	04.76	04.37	93.79	08.86	98.09
71.5	64.41	53.40	14.64	03.72	03.32	92.66	07.74	96.99
72.5	63.53	52.31	13.71	02.66	02.32	91.46	06.66	95.82
73.5	62.50	51.27	12.75	01.53	01.26	90.22	05.53	94.43
74.5	61.53	50.14	11.70	00.39	00.21	89.02	04.46	93.13
75.5	60.62	49.01	10.79	20699.23	20999.18	87.80	03.24	91.87
76.5	59.53	47.92	09.81	98.10	98.09	86.61	02.16	90.66
77.5	58.62	46.75	08.83	96.96	96.97	85.33	00.95	89.35
78.5	57.53	45.53	07.84	95.80	95.85	84.06	21199.82	88.01
79.5	56.53	44.36	06.86	94.63	94.82	82.73	98.66	86.53
80.5	55.43	43.20	05.79	93.48	93.53	81.50	97.44	85.20

TABLE II (continued)

J	3 - 2		3 - 2		4 - 2		4 - 1	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
81.5	20384.10	20341.62	20704.69	20692.21	20992.34	20955.10	21196.87	21183.92
82.5	53.20	47.75	03.59	91.05	91.10	73.30	95.05	82.62
83.5	52.10	39.49	02.55	89.92	89.96	77.49	93.76	81.32
84.5	51.09	33.32	01.45	88.64	88.70	76.17	92.50	79.93
85.5	49.96	30.97	00.33	87.30	87.34	74.04	91.20	78.50
86.5	48.30	25.67	20699.22	86.11	87.23	73.45	89.89	77.15
87.5	47.70	24.50	98.10	84.87	84.95	71.99	88.59	75.80
88.5	46.50	23.24	96.90	83.54	83.67	70.63	87.29	-
89.5	45.36	21.76	95.75	82.22	82.31	69.12	85.99	
90.5	44.10	20.37	94.50	80.89	80.93	67.60	84.64	
91.5	42.97	18.00	93.39	79.56	79.63	66.10	83.25	
92.5	41.75	17.60	92.15	78.15	78.30	64.60	81.86	
93.5	40.45	16.25	90.91	76.78	76.93	63.00	80.56	
94.5	39.20	14.90	89.66	75.46	75.54	61.46	79.12	
95.5	38.01	13.52	88.38	74.01	74.13	59.89	77.63	
96.5	36.62	12.09	87.14	72.55	72.70	58.36	76.23	
97.5	35.41	10.70	85.83	71.14	71.20	-	74.81	
98.5	34.15	19.10	84.57	69.69	69.71		-	
99.5	32.70	17.75	83.24	68.22	68.26			

TABLE II (continued)

J	3 - 2 R(J)	3 - 2 P(J)	2 - 2 R(J)	2 - 2 P(J)	4 - 2 R(J)	4 - 2 P(J)	4 - 1 R(J)	4 - 1 P(J)
100.5	20201.54	20015.37	20601.02	20446.73	20960.20	—	—	—
101.5	00.13	14.30	00.63	65.03	65.31	—	—	—
102.5	00.31	10.46	79.27	00.34	60.01			
103.5	07.46	11.77	77.90	60.06	60.32			
104.5	00.03	10.21	76.53	60.60	60.07			
105.5	04.09	00.05	75.16	00.19	00.20			
106.5	03.30	07.05	73.71	57.60	57.66			
107.5	01.72	05.50	72.00	56.00	-			
108.5	00.40	04.00	70.34	54.40				
109.5	59.05	00.33	69.00	52.70				
110.5	57.62	00.60	67.93	51.24				
111.5	16.10	20799.13	66.44	49.51				
112.5	14.31	97.40	64.99	47.96				
113.5	12.04	95.79	03.45	46.30				
114.5	11.00	94.15	61.96	44.72				
115.5	09.00	92.55	60.42	42.76				
116.5	08.00	90.70	50.92	41.01				
117.5	06.74	09.09	57.05	39.55				
118.5	05.10	07.00	55.60	37.06				

TABLE II (continued)

J	3 - 2		2 - 2		3 - 2		4 - 1	
	R(J)	P(J)	R(J)	P(J)				
119.5	20303.53	20705.03	20654.32	20581.11	—	—	—	—
120.5	01.94	03.73	52.35	34.26	—	—	—	—
121.5	00.34	02.30	50.09	32.43				
122.5	20700.57	00.19	49.57	30.69				
123.5	97.20	78.42	47.45	28.37				
124.5	95.53	76.61	45.38	27.07				
125.5	93.53	74.79	44.04	25.24				
126.5	92.03	72.94	42.46	23.37				
127.5	90.39	71.12	40.75	21.56				
128.5	88.70	69.27	39.05	19.75				
129.5	86.97	67.37	37.39	17.34				
130.5	85.25	65.47	35.64	15.38				
131.5	83.47	63.57	34.02	14.01				
132.5	81.74	61.63	32.11	12.01				
133.5	79.97	59.69	30.32	10.20				
134.5	78.16	-	28.45	-				
135.5	76.35		26.70					
136.5	74.49		24.83					
137.5	72.60		23.04					

TABLE XIII. Vacuum Wavenumbers and Rotational Assignments for (3, 2) and (2, 2) bands of $Rb^{81}Br$ molecule.

J	3 - 2		2 - 2	
	R(J)	P(J)	R(J)	P(J)
9.5		20090.63		
10.5		89.41		
11.5		88.15		
12.5		86.88		
13.5		85.67		
14.5		84.36		
15.5		83.09		
16.5		81.79		
17.5		80.44		
18.5		79.14		
19.5		77.74		
20.5	20093.63	76.40		
21.5	92.41	75.05		
22.5	91.15	73.65		
23.5	89.88	72.26		
24.5	88.67	70.87		20740.31
25.5	87.36	69.43		39.00
26.5	86.05	68.00		39.45
27.5	84.79	66.47		39.02
28.5	83.44	65.03		38.55
29.5	82.14	63.59	—	37.99
30.5	80.74	62.07	—	37.34

TABLE III (Continued)

J	R(J) $^{3}-^{2}$ P(J)		Q(J) $^{2}-^{2}$ P(J)	
31.5	20300.40	20303.51		20736.96
32.5	00.05	09.00		36.44
33.5	09.65	04.46		35.93
34.5	09.26	03.89		35.32
35.5	08.07	03.37	20740.31	34.81
36.5	08.43	02.76	39.03	34.33
37.5	08.00	02.15	39.48	33.73
38.5	07.47	01.58	39.02	33.09
39.5	07.03	00.97	38.55	32.44
40.5	06.55	00.36	37.90	31.67
41.5	86.07	79.71	37.34	31.02
42.5	05.51	79.01	36.79	30.29
43.5	05.03	78.40	36.27	29.73
44.5	04.46	77.70	35.71	28.92
45.5	03.89	77.00	35.15	28.27
46.5	03.37	76.26	34.61	27.54
47.5	02.76	75.52	34.00	26.73
48.5	02.15	74.82	33.43	25.91
49.5	01.58	74.04	32.74	25.10
50.5	00.97	73.30	32.10	24.41
51.5	00.36	72.56	31.45	23.63
52.5	79.71	71.69	30.81	22.77
53.5	79.01	70.90	30.16	21.96
54.5	78.40	78.07	29.43	21.14

TABLE III (Continued)

J	R(J)	P(J)	R(J)	P(J)
55.5	20077.70	20069.25	20720.75	20000.20
56.5	77.00	60.42	20.06	19.42
57.5	76.26	67.59	27.24	10.56
58.5	75.52	66.60	26.47	17.66
59.5	74.02	65.00	25.69	16.66
60.5	74.04	64.09	24.96	15.76
61.5	73.30	63.93	24.15	14.06
62.5	72.56	62.97	20.37	13.91
63.5	71.69	62.06	22.56	12.95
64.5	70.90	61.15	21.74	12.03
65.5	70.07	60.10	20.93	11.04
66.5	69.25	59.14	20.07	10.05
67.5	68.42	58.14	19.21	09.03
68.5	67.59	57.14	18.31	08.04
69.5	66.63	56.23	17.40	06.92
70.5	65.80	55.19	16.49	05.31
71.5	64.79	54.14	15.57	04.76
72.5	63.93	52.97	14.64	03.72
73.5	62.97	51.96	13.71	02.66
74.5	62.06	50.83	12.75	01.55
75.5	61.15	49.79	11.70	00.33
76.5	60.10	48.62	10.79	20099.22
77.5	59.14	47.53	09.81	98.10
78.5	58.14	46.36	08.83	96.90

TABLE III (Continued)

J	R(J)	P(J)	R(J)	P(J)
79.5	20057.14	20045.23	20707.04	20695.75
80.5	56.05	44.05	06.84	94.59
81.5	55.01	42.84	05.56	93.39
82.5	53.92	41.59	04.53	92.15
83.5	52.78	40.45	03.59	90.91
84.5	51.75	39.23	02.43	89.66
85.5	50.70	38.01	01.27	88.38
86.5	49.62	36.62	00.07	87.14
87.5	48.49	35.41	20699.96	85.85
88.5	47.31	34.15	97.85	84.57
89.5	46.10	32.80	96.69	83.24
90.5	45.01	31.54	95.49	81.92
91.5	43.84	30.15	94.29	80.63
92.5	42.62	28.91	93.13	79.27
93.5	41.44	27.46	91.93	77.90
94.5	40.19	26.00	90.69	76.53
95.5	38.97	24.69	89.41	75.16
96.5	37.71	23.39	88.17	73.71
97.5	36.45	21.82	86.84	72.30
98.5	35.19	20.48	85.56	70.84
99.5	33.89	19.05	84.23	69.39
100.5	32.59	17.62	82.90	67.90
101.5	31.28	16.10	81.62	66.42
102.5	29.98	14.61	80.33	64.99

TABLE III (Continued)

J	R(J)	P(J)	R(J)	P(J)
103.5	20328.59	20813.24	20679.01	20663.45
104.5	27.20	11.77	77.60	61.96
105.5	25.36	10.21	76.19	60.42
106.5	24.43	00.65	74.90	59.02
107.5	23.00	07.09	73.36	57.35
108.5	21.56	05.53	72.00	55.70
109.5	20.51	00.98	70.54	54.11
110.5	19.08	02.33	69.19	52.57
111.5	17.40	00.67	67.64	50.99
112.5	15.93	20799.13	66.14	49.38
113.5	14.46	97.40	64.62	47.70
114.5	12.94	95.79	63.19	46.04
115.5	11.30	94.15	61.66	44.42
116.5	09.82	92.55	60.16	42.76
117.5	08.30	90.78	58.63	41.01
118.5	06.74	89.09	57.09	39.35
119.5	05.10	87.36	55.42	37.60
120.5	03.58	85.60	53.67	35.90
121.5	01.94	83.99	52.19	34.12
122.5	00.24	82.22	50.52	32.32
123.5	20798.67	80.49	49.07	30.53
124.5	97.02	78.64	47.32	28.74
125.5	95.58	76.91	45.83	26.91
126.5	93.96	75.35	44.02	25.09

TABLE XII (Continued)

J	R(J)	P(J)	R(J)	P(J)
127.5	20792.03	20773.20	20640.12	20622.30
128.5	90.39	71.30	40.54	21.47
129.5	88.83	69.57	38.79	19.55
130.5	87.14	67.71	37.09	17.50
131.5	85.50	66.02	35.24	15.77
132.5	83.70	64.02	33.50	13.96
133.5	82.03	62.02	31.79	11.94
134.5	80.16	60.12	30.00	10.03
135.5	78.42	58.20	28.19	08.16
136.5	76.61	56.30	26.38	06.21
137.5	74.79	54.31	24.57	04.13
138.5	72.94	52.20	22.78	02.09
139.5	71.12	-	20.90	-
140.5	69.27		19.17	
141.5	67.37		18.32	
142.5	65.47		-	
143.5	63.57			
144.5	61.63			
145.5	59.69			

rotational term $F_v(J)$ we arrive at the relation,

$$\Delta_2 F_v(J) = F_v(J+1) - F_v(J-1)$$

$$= (4B_v - 6D_v)(J+\tfrac{1}{2}) - 8D_v(J+\tfrac{1}{2})^3 \quad \ldots\ldots(5)$$

Since D_v is a very small quantity as compared to B_v,

$$\Delta_2 F_v(J) = 4B_v(J+\tfrac{1}{2}) \quad \ldots\ldots\ldots\ldots(6)$$

or $$\frac{\Delta_2 F(J)}{(J+\tfrac{1}{2})} = 4B_v \quad \ldots\ldots\ldots\ldots(7)$$

A plot of $\Delta_2 F(J)$ against J would give a straight line. The slope of this line gives the value of $4B_v$. A preliminary J numbering of the branches is obtained and the curve is plotted. To obtain the correct J numbering the abscissa scale is shifted until this straight line cuts the abscissa at $x = -\tfrac{1}{2}$.

In case of heavy molecules it is often not possible to get zero gap clearly marked out on the plate and the numbering of the lines is not often unambiguous. However, it becomes possible to find out the J numbering of the rotational lines if more than one band with the same v' or v'' are measured, because for the common vibrational level the combination differences must agree exactly for

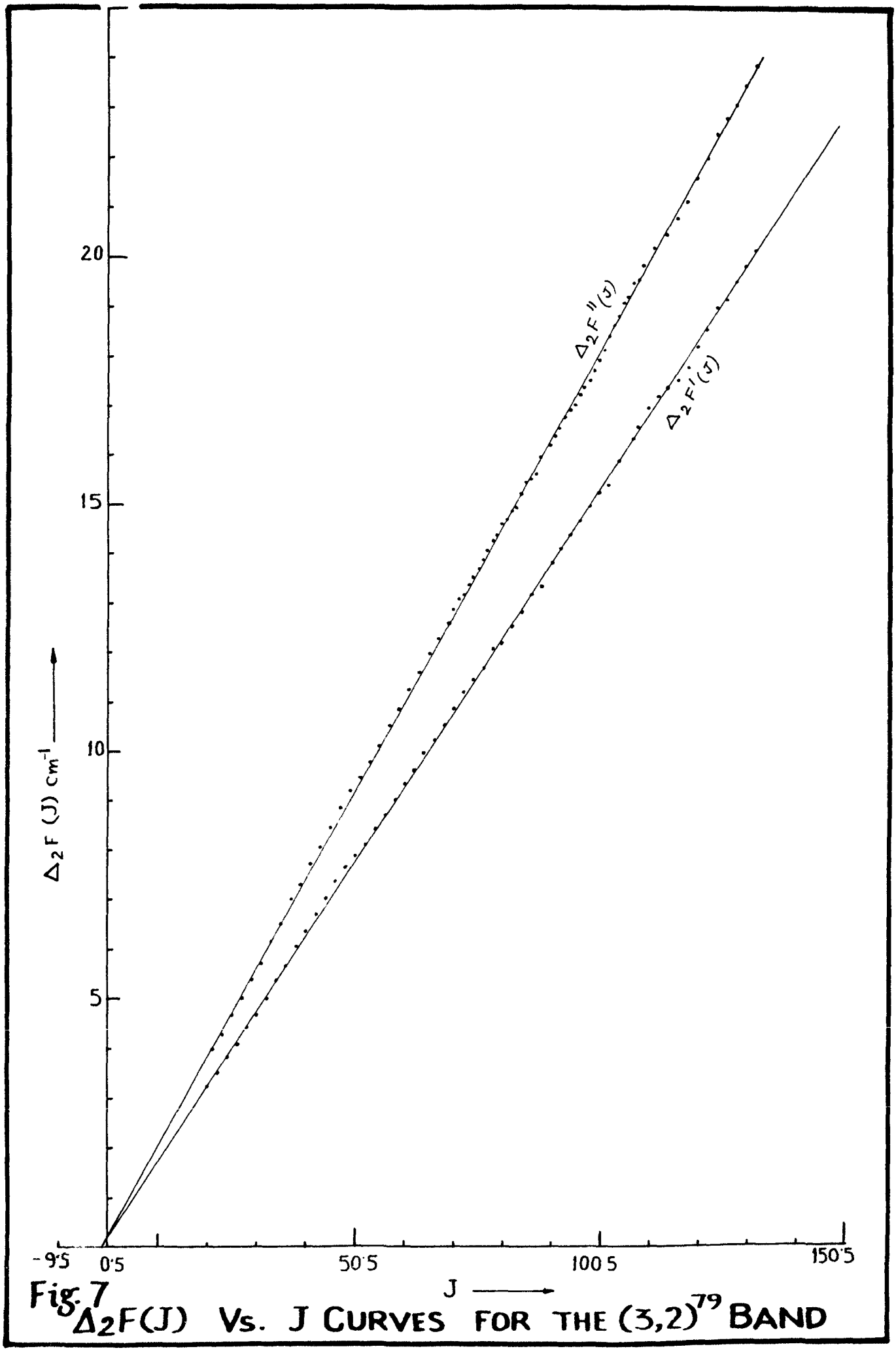

Fig. 7 $\Delta_2 F(J)$ Vs. J CURVES FOR THE $(3,2)^{79}$ BAND

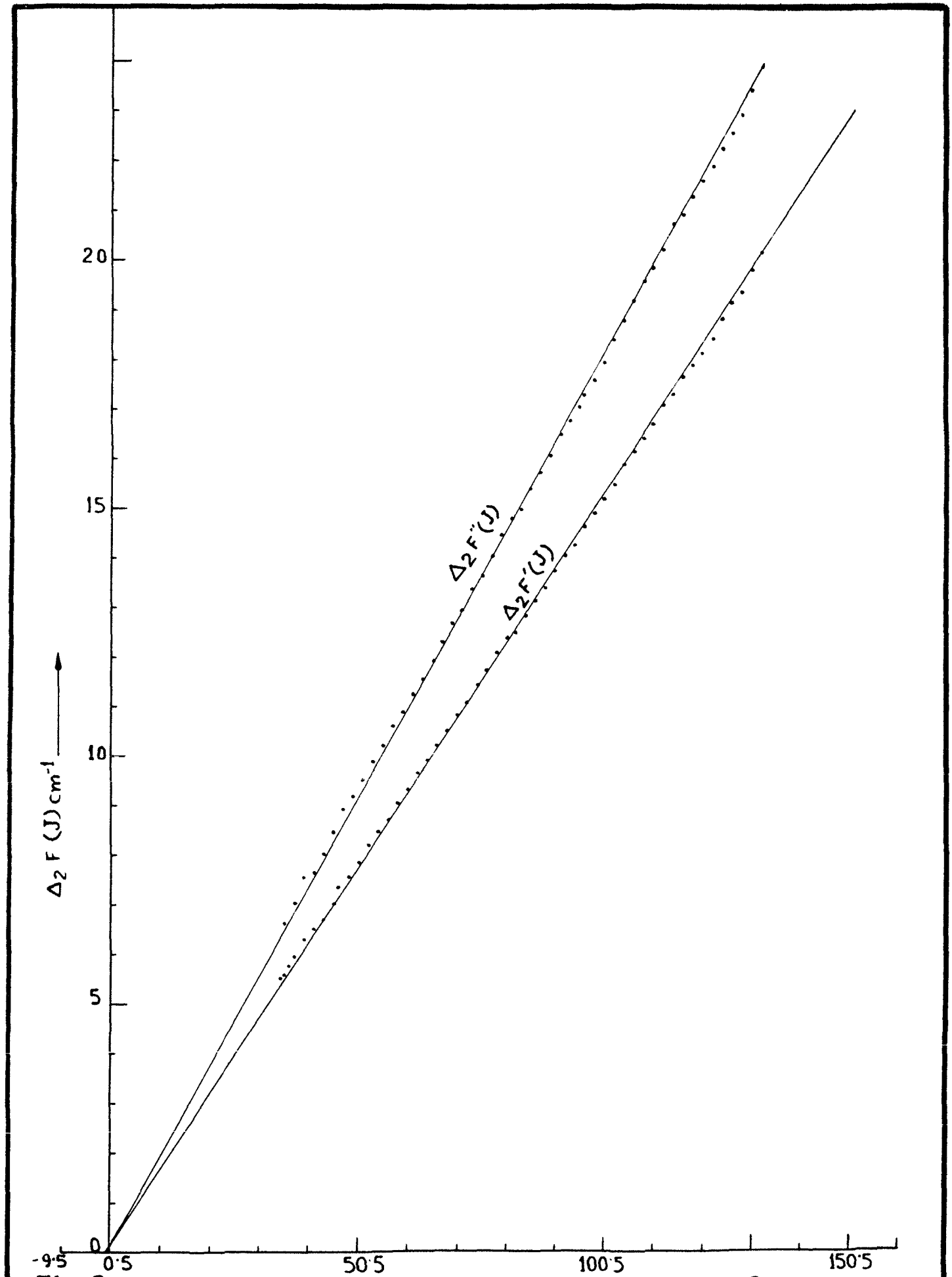

Fig. 8 $\Delta_2 F(J)$ Vs. J CURVES FOR THE $(2,2)^{79}$ BAND

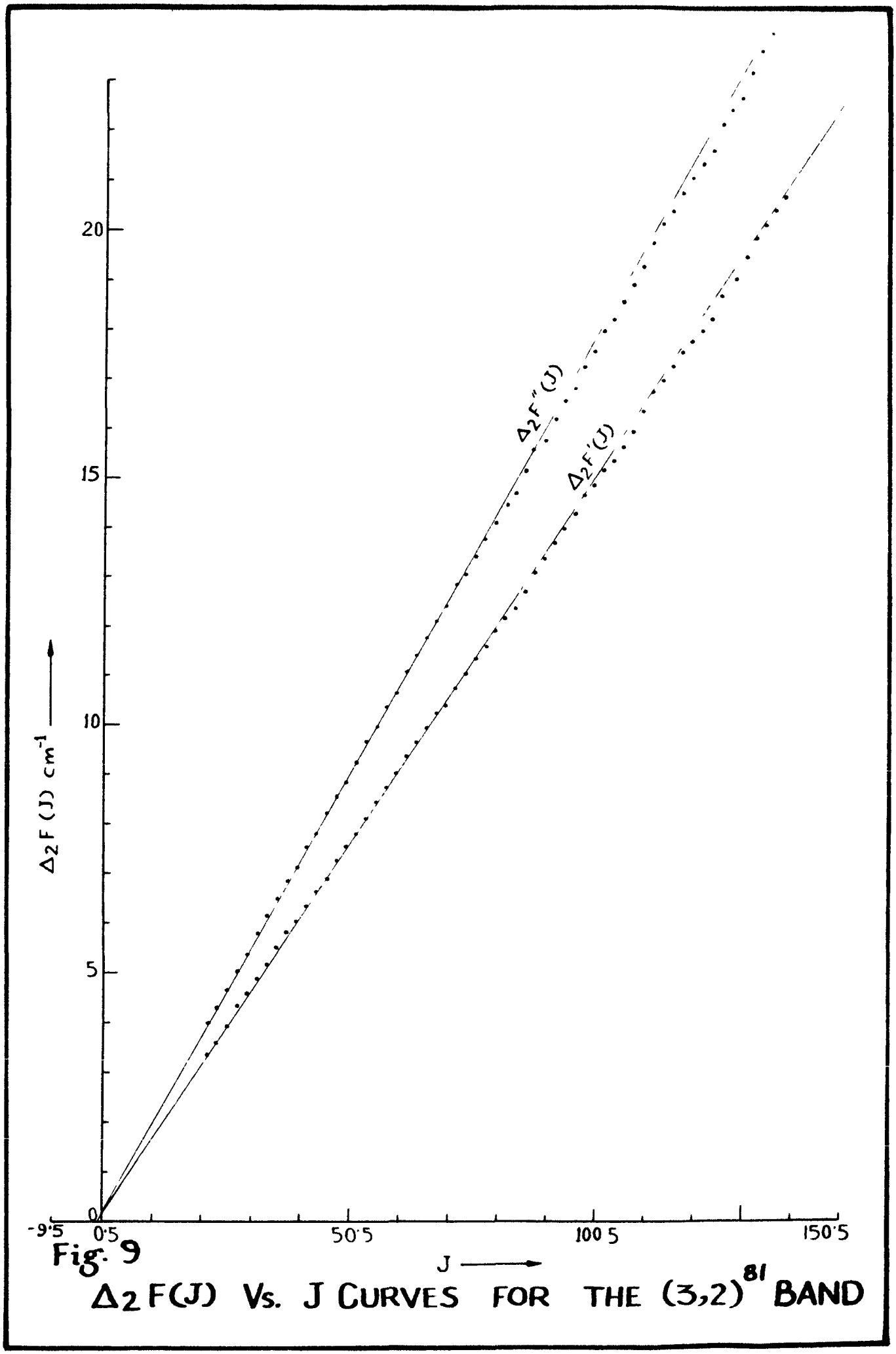

Fig. 9

$\Delta_2 F(J)$ Vs. J CURVES FOR THE $(3,2)^{81}$ BAND

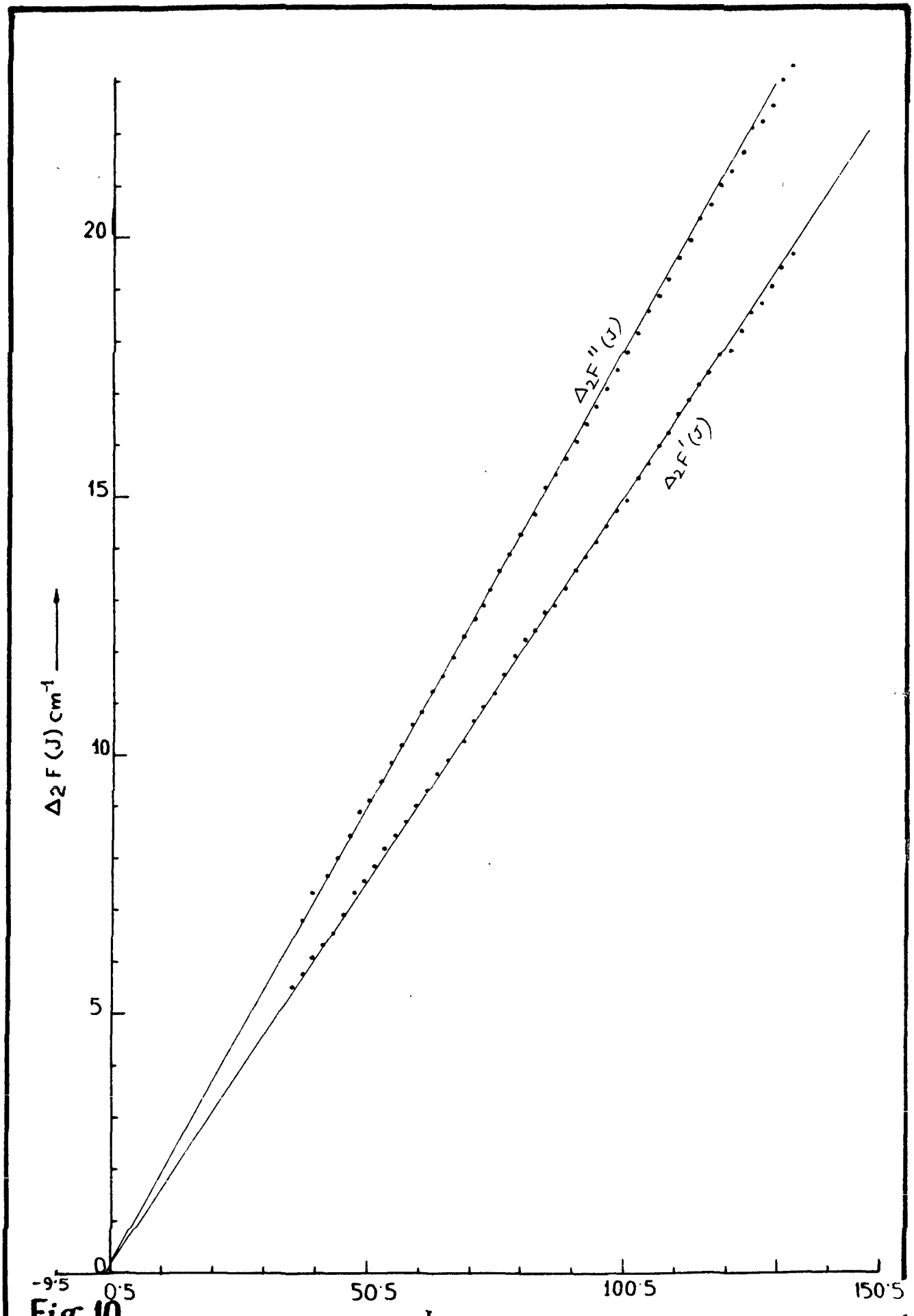

Fig. 10 $\Delta_2 F(J)$ Vs. J CURVES FOR THE $(2,2)^{81}$ BAND

each J value. Thus the relative numbering for the rotational lines of bands with common upper (or lower) vibrational level can be obtained by comparing the combination differences. To start with; the bands (3, 2), (2, 2) and (4, 2) were taken up. Since these bands have a common lower vibrational level $v'' = 2$, with a preliminary J numbering the combination differences $\Delta_2F''(J)$ were obtained for each of the bands. The three sets of $\Delta_2F''(J)$ values were compared together and the J numbering in one of the branches of each band was changed by 1 or 2 units. Finally an arrangement of the various sets of $\Delta_2F''(J)$ values was obtained after a few trials, to match within the limits of experimental error. Thus the correct relative numbering was fixed for the bands (3, 2), (2, 2) and (4, 2). Similarly the relative numbering for the band (4, 1) was obtained by comparing its upper state combination differences $\Delta_2F'(J)$ with that of the (4, 2) band.

To arrive at the absolute numbering, $\Delta_2F(J)$ values were plotted against a preliminary numbering and the abscissa scale was shifted so that the straight lines go through the point $x = -\frac{1}{2}$ (Figs.9 to 10). The combination differences for all the bands are collected in Tables IV and V.

TABLE IV

The combination differences for the (3, 2), (2, 2), (4, 2) and (4, 1) bands of the $Pb^{79}Br$ molecule in cm^{-1}.

J	3 - 2		2 - 2		4 - 2		4 - 1	
	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
20.5	3.23							
21.5	3.36	3.98						
22.5	3.50	4.15						
23.5	3.62	4.28						
24.5	3.00	4.45						
25.5	3.93	4.67						
26.5	4.05	4.09						
27.5	4.22	5.02						
28.5	4.41	5.24						
29.5	4.59	5.37						
30.5	4.67	5.63						
31.5	4.09	5.71						
32.5	5.02	5.94						
33.5	5.19	6.16						
34.5	5.37	6.28	5.50	-				
35.5	5.50	6.50	5.55	6.58				
36.5	5.67	6.72	5.72	6.79				
37.5	5.85	7.02	5.93	7.01	—	—	—	—
38.5	6.06	7.16	6.11	7.35	—	—	—	—

TABLE IV (continued)

J	3 - 2		2 - 2		4 - 2		4 - 1	
39.5	6.19	7.20	6.32	7.33				
40.5	6.36	7.54	6.32	7.70				
41.5	6.50	7.72	6.50	7.61				
42.5	6.63	7.93	6.54	7.37	-	-	6.53	-
43.5	6.09	8.07	6.79	8.00	6.00	-	6.00	8.30
44.5	7.02	8.29	6.93	8.17	6.08	8.39	6.90	8.43
45.5	7.15	8.46	7.07	8.42	7.04	8.50	7.04	8.50
46.5	7.37	8.63	7.35	8.70	7.20	8.72	7.20	8.68
47.5	7.50	8.85	7.42	8.90	7.32	8.90	7.30	8.93
48.5	7.63	9.03	7.56	9.02	7.30	9.04	7.43	9.11
49.5	7.60	9.20	7.69	9.11	7.49	9.11	7.57	9.29
50.5	7.09	9.20	7.02	9.33	7.71	9.27	7.81	9.52
51.5	7.98	9.46	8.04	9.49	7.94	9.47	8.00	9.70
52.5	8.11	9.59	8.20	9.67	8.03	9.74	8.08	9.90
53.5	8.23	9.77	8.29	9.83	8.17	9.88	8.25	10.10
54.5	8.42	9.98	8.47	10.01	8.29	10.07	8.43	10.24
55.5	8.59	10.11	8.64	10.19	8.48	10.29	8.57	10.32
56.5	8.71	10.33	8.80	10.40	8.61	10.38	8.75	10.56
57.5	8.89	10.50	8.81	10.58	8.79	10.46	8.82	10.69
58.5	9.02	10.69	9.03	10.71	8.78	10.73	8.99	10.88
59.5	9.15	10.85	9.22	10.83	8.83	10.78	8.93	10.98
60.5	9.32	11.02	9.39	11.05	9.23	10.95	9.32	11.25
61.5	9.45	11.23	9.46	11.22	9.40	11.30	9.39	11.44

TABLE IV (continued)

J	0 - 2		2 - 2		4 - 2		4 - 1	
62.5	9.71	11.37	9.60	11.34	9.49	11.52	9.64	11.75
63.5	9.80	11.59	9.71	11.52	9.53	11.74	9.31	11.63
64.5	9.93	11.80	9.89	11.69	9.84	11.79	9.90	12.06
65.5	10.14	11.93	10.02	11.90	9.93	11.96	10.12	12.24
66.5	10.23	12.14	10.10	12.03	10.15	12.13	10.21	12.41
67.5	10.45	12.23	10.27	12.29	10.28	12.35	10.34	12.46
68.5	10.49	12.45	10.40	12.50	10.36	12.57	10.39	12.64
69.5	10.66	12.50	10.60	12.64	10.49	12.66	10.57	12.80
70.5	10.84	12.84	10.81	12.77	10.58	12.74	10.47	12.86
71.5	11.01	13.06	10.92	12.91	10.67	12.91	10.75	13.04
72.5	11.19	13.14	11.05	13.09	10.86	13.10	10.84	13.31
73.5	11.29	13.36	11.20	13.32	11.04	13.30	11.15	13.50
74.5	11.44	13.49	11.39	13.40	11.19	13.46	11.33	13.71
75.5	11.61	13.66	11.52	13.50	11.30	13.60	11.37	13.80
76.5	11.66	13.87	11.71	13.83	11.47	13.85	11.50	13.89
77.5	11.87	14.05	11.87	14.01	11.64	14.02	11.60	14.15
78.5	12.05	14.26	12.04	14.20	11.79	14.19	11.81	14.42
79.5	12.17	14.35	12.21	14.42	12.04	14.35	12.13	14.60
80.5	12.17	14.61	12.37	14.63	12.00	14.64	12.22	14.74
81.5	12.44	14.65	12.48	14.74	12.16	14.70	12.35	14.82
82.5	12.48	14.87	12.40	14.77	12.27	14.85	12.44	14.95
83.5	12.69	14.91	12.63	14.15	12.47	14.93	12.44	15.13
84.5	12.77	15.21	12.81	15.17	12.61	15.12	12.57	15.18

TABLE IV (continued)

J	3 - 2		2 - 2		4 - 2		4 - 1	
85.5	12.99	15.42	12.95	15.34	12.70	15.33	12.62	15.35
86.5	13.16	15.46	13.11	15.46	12.78	15.55	12.74	15.40
87.5	13.20	15.51	13.23	15.63	12.96	15.60	12.79	15.52
88.5	13.29	15.94	13.36	15.83	12.94	15.83	-	-
89.5	13.60	16.16	13.53	16.01	13.11	16.04		
90.5	13.81	16.33	13.70	16.19	13.30	16.23		
91.5	13.94	16.50	13.83	16.44	13.45	16.30		
92.5	14.07	16.72	14.00	16.61	13.69	16.60		
93.5	14.20	16.85	14.13	16.69	13.90	16.74		
94.5	14.33	16.93	14.20	16.90	14.03	16.94		
95.5	14.49	17.14	14.37	17.11	14.24	17.10		
96.5	14.53	17.31	14.39	17.24	14.34	-		
97.5	14.71	17.44	14.71	17.45	-	-		
98.5	14.97	17.66	14.83	17.63				
99.5	15.05	17.83	14.92	17.79				
100.5	15.22	18.03	15.14	17.91				
101.5	15.35	18.08	15.30	18.08				
102.5	15.35	18.30	15.43	18.37				
103.5	15.69	18.68	15.64	18.59				
104.5	15.87	18.81	15.85	18.72				
105.5	16.04	19.03	15.98	18.93				
106.5	16.34	19.16	16.11	19.14				
107.5	16.39	19.46	16.29	19.23				
108.5	16.55	19.49	16.35	19.52				

TABLE IV (continuod)

J	3 - 2		2 - 2		4 - 2		4 - 1	
109.5	16.72	19.00	16.61	19.00	—	—	—	—
110.5	16.94	19.92	16.04	19.81	—	—	—	—
111.5	16.97	20.14	16.06	20.02				
112.5	17.13	20.31	17.08	20.14				
113.5	17.15	20.46	17.15	20.27				
114.5	17.23	[illegible]	17.24	20.09				
115.5	17.27	20.60	17.06	20.08				
116.5	17.52	20.73	17.61	20.07				
117.5	17.68	20.94	17.80	21.06				
118.5	17.74	21.06	17.82	21.24				
119.5	17.90	21.32	17.91	21.42				
120.5	18.16	21.58	18.09	21.54				
121.5	18.34	21.75	18.27	21.66				
122.5	18.40	21.92	18.30	21.82				
123.5	18.00	22.06	18.53	22.00				
124.5	18.97	22.43	18.76	22.21				
125.5	19.05	22.64	18.90	22.46				
126.5	19.09	22.73	19.09	22.43				
127.5	19.27	22.76	19.19	22.71				
128.5	19.43	23.02	19.30	22.91				
129.5	19.60	23.23	19.55	23.17				
130.5	19.73	23.40	19.73	23.33				
131.5	19.90	23.62	20.01	23.62				
132.5	20.11	23.76	20.10	23.82				

TABLE V: The Combination Differences for the (3, 2) and (2, 2) bands of the $Pb^{81}Br$ molecule in wavenumbers.

J	3 - 2		2 - 2	
	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
21.5	3.36	3.93		
22.5	3.50	4.15		
23.5	3.62	4.20		
24.5	3.80	4.45		
25.5	3.93	4.67		
26.5	4.04	4.89		
27.5	4.23	5.02		
28.5	4.41	5.24		
29.5	4.59	5.37		
30.5	4.67	5.63		
31.5	4.89	5.71		
32.5	5.02	5.94		
33.5	5.19	6.16		
34.5	5.37	6.28		
35.5	5.50	6.50	5.50	
36.5	5.67	6.72	5.55	6.53
37.5	5.85	6.85	5.72	6.79
38.5	5.99	7.00	5.93	7.01
39.5	6.06	7.11	6.11	7.35
40.5	6.19	7.32	6.32	7.53
41.5	6.36	7.54	6.32	7.70
42.5	6.50	7.67	6.50	7.61

TABLE V(Continued)

J	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
43.5	6.63	7.01	6.54	7.37
44.5	6.76	0.03	6.79	0.00
45.5	6.89	0.20	6.90	0.17
46.5	7.11	0.37	7.07	8.42
47.5	7.24	0.55	7.35	0.70
48.5	7.30	0.72	7.52	0.90
49.5	7.54	0.38	7.56	9.32
50.5	7.67	9.02	7.69	9.11
51.5	7.80	9.28	7.82	9.30
52.5	8.02	9.46	8.04	9.49
53.5	8.11	9.64	8.20	9.67
54.5	8.33	9.76	8.39	9.30
55.5	8.45	9.93	8.47	10.01
56.5	8.58	10.11	8.64	10.19
57.5	8.67	10.37	8.80	10.40
58.5	8.89	10.46	8.81	10.58
59.5	9.02	10.63	9.03	10.71
60.5	9.15	10.89	9.20	10.88
61.5	9.40	11.07	9.39	11.05
62.5	9.59	11.24	9.46	11.22
63.5	9.63	11.41	9.63	11.34
64.5	9.75	11.59	9.71	11.52
65.5	9.97	11.76	9.89	11.69

TABLE V (Continued)

J	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
66.5	10.11	11.93	10.02	11.99
67.5	10.20	12.11	10.18	12.03
68.5	10.45	12.19	10.37	12.29
69.5	10.40	12.41	10.48	12.50
70.5	10.62	12.49	10.60	12.64
71.5	10.75	12.63	10.81	12.77
72.5	10.96	12.93	10.92	12.91
73.5	11.01	13.05	11.05	13.09
74.5	11.10	13.10	11.20	13.33
75.5	11.36	13.44	11.45	13.53
76.5	11.40	13.62	11.57	13.60
77.5	11.61	13.74	11.71	13.89
78.5	11.70	13.91	11.93	14.06
79.5	11.91	14.09	12.09	14.24
80.5	12.00	14.33	12.25	14.45
81.5	12.17	14.47	12.17	14.69
82.5	12.34	14.56	12.30	14.65
83.5	12.33	14.69	12.60	14.87
84.5	12.52	14.77	12.77	15.21
85.5	12.69	15.13	12.89	15.29
86.5	13.00	15.29	12.93	15.43
87.5	13.03	15.47	13.11	15.50
88.5	13.16	15.69	13.23	15.72
89.5	13.37	15.77	13.45	15.93

TABLE V (Continued)

J	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
90.5	13.47	16.03	13.57	16.06
91.5	13.69	16.20	13.66	16.22
92.5	13.81	16.38	13.86	16.39
93.5	13.93	16.54	14.03	16.60
94.5	14.11	16.75	14.12	16.77
95.5	14.20	16.90	14.25	16.94
96.5	14.32	17.15	14.46	17.11
97.5	14.63	17.20	14.54	17.33
98.5	14.71	17.40	14.72	17.45
99.5	14.84	17.57	14.84	17.58
100.5	14.97	17.79	14.92	17.79
101.5	15.10	17.90	15.10	17.91
102.5	15.37	18.04	15.34	18.17
103.5	15.35	18.21	15.56	18.37
104.5	15.43	18.38	15.64	18,59
105.5	15.65	18.55	15.77	18.68
106.5	15.78	18.81	15.98	18.84
107.5	15.95	18.90	16.01	19.12
108.5	16.03	19.07	16.22	19.17
109.5	16.33	19.23	16.35	19.43
110.5	16.55	19.63	16.61	19.55
111.5	16.73	19.75	16.65	19.86
112.5	16.80	19.92	16.80	19.94
113.5	16.93	20.14	17.12	20.10

TABLE V (Continued)

J	$\Delta_2 F'$	$\Delta_2 F''$	$\Delta_2 F'$	$\Delta_2 F''$
114.5	17.15	20.31	17.15	20.40
115.5	17.23	20.39	17.24	20.48
116.5	17.27	20.60	17.40	20.65
117.5	17.52	20.73	17.62	20.81
110.5	17.69	20.94	17.74	21.03
119.5	17.74	21.06	17.82	21.19
120.5	17.90	21.11	17.77	21.30
121.5	17.95	21.30	18.07	21.35
122.5	18.02	21.49	18.20	21.66
123.5	18.22	21.69	18.34	21.70
124.5	18.30	21.76	18.50	22.16
125.5	18.67	22.17	18.62	22.24
126.5	18.80	22.30	18.74	22.2[illegible]
127.5	18.75	22.47	18.82	22.35
128.5	19.01	22.46	19.07	22.57
129.5	19.26	22.68	19.24	22.86
130.5	19.43	23.01	19.41	23.02
131.5	19.[illegible]3	23.22	19.47	23.23
132.5	19.86	23.43	19.69	23.30
133.5	19.93	23.66	19.85	23.52
134.5	20.07	23.77	19.97	23.69
135.5	20.19	23.99	20.20	23.79
136.5	20.41	24.11	20.17	24.06
137.5	2[illegible].43	24.33	20.44	24.29

DETERMINATION OF ROTATIONAL CONSTANTS

The rotational constants were obtained following the usual procedure (Rosenberg[11]). As the D_v values are very small the D_v values were obtained plotting the $\Delta_2 F(J)$ values against J. The curve is almost a straight line and the slope of the line gives $4D_v$. For the vibrational levels common to two or more bands the average of the D_v values has been taken (Table VI). From the values of D_v' and D_v'', the constants D_o' and D_o'' as well as α_e' and α_e'' are calculated using the relation

$$D_v = D_o - \alpha_o(v + \tfrac{1}{2}) \qquad \ldots\ldots\ldots\ldots(8)$$

and are listed in Table VII. As only four bands have been analysed the α_o values are approximate ones. The observed value of α_o agrees very well with the calculated value (Table VII) obtained from the relation:

$$\alpha_o = \frac{6(\omega_e x_e D_e^3)^{\frac{1}{2}}}{\omega_e} - \frac{6 D_e^2}{\omega_e} \qquad \ldots\ldots\ldots(9)$$

The values of r_o' and r_o'' are then obtained from the relation:

$$r_o = \frac{4.1061}{(\mu_A D_o)^{\frac{1}{2}}} \text{ Å} \qquad \ldots\ldots\ldots(10)$$

TABLE VI

The B_v' and B_v'' values of the different bands studied.

	$Pb^{79}Br$		$Pb^{81}Br$	
v' v''	B_v' cm^{-1}	B_v'' cm^{-1}	B_v' cm^{-1}	B_v'' cm^{-1}
2, 2	0.0382_0	0.0431_5	0.0374_0	0.0442_0
3, 2	0.0380_5	0.0431_0	0.0372_5	0.0442_0
4, 2	0.0379_0	0.0431_0	-	-
4, 1	0.0379_0	0.0432_5	-	-

TABLE VII

The molecular constants obtained for PbBr.

	$Pb^{79}Br$	$Pb^{81}Br$
B_e'	0.0385 cm^{-1}	0.0378 cm^{-1}
B_e''	0.0455 cm^{-1}	0.0446 cm^{-1}
r_e'	$2.76_8 \times 10^{-8}$ cm	$2.76_6 \times 10^{-8}$ cm
r_e''	$2.54_6 \times 10^{-8}$ cm	$2.54_5 \times 10^{-8}$ cm

	Observed	Calculated
α_e'	= 0.00015 cm^{-1}	0.000129 cm^{-1}
α_e''	= 0.00015 cm^{-1}	0.00014 cm^{-1}
D_4'	$\simeq 2 \times 10^{-8}$ cm^{-1}	$D_e' = 0.99 \times 10^{-8}$ cm^{-1}
D_2''	$\simeq 1 \times 10^{-8}$ cm^{-1}	$D_e'' = 0.88 \times 10^{-8}$ cm^{-1}

where $\mu_A = 97.227$ for $^{208}Pb^{79}Br$

and $\mu_A = 98.270$ for $^{208}Pb^{81}Br$.

These values are included in Table VII.

An attempt was made to obtain the D_v values from the $\Delta_2F/(J+\frac{1}{2})$ versus $(J+\frac{1}{2})^2$ curves and to determine the D_v values more accurately therefrom. Because of the limit of our accuracy, the points are quite random and a straight line could not be drawn. However, taking an average of the three sets of $\Delta_2F''(J)$ values for the vibrational level $v'' = 2$, from (3, 2), (2, 2) and (4, 2) bands and $\Delta_2F''(J)$ values for $v' = 4$ from (4, 2) and (4, 1) bands the randomness of the points was reduced. The D values obtained are:

$$D_4' = 2 \times 10^{-8} \text{ cm}^{-1} \; ; \quad D_2'' = 1 \times 10^{-8} \text{ cm}^{-1}$$

The calculated value of D_0'' from the relation (2) is 0.9×10^{-8} cm^{-1}.

THE ELECTRONIC TRANSITION INVOLVED

The fact, that the rotational structure of the bands contains only the P and R branches, shows that the transition involved is either a $\Sigma - \Sigma$ if Hund's case (a) or (b) type coupling holds good or a 0–0 if Hund's case (c) type coupling is valid. The present band system has been

observed in emission as well as in absorption, which implies that the lower state of this system is the ground state of the PbBr molecule.

The electronic term schemes of the monohalides of silicon, tin and lead are expected to be similar to one another. We shall discuss here in brief the electronic term scheme for the PbBr molecule. As the molecule is heavy, it is sufficient for practical purposes to consider the electrons outside the filled shells. The lowest electronic configurations for the two atoms are :

$$Pb \text{ —— } (KLMNO_{spd})\ 6s^2\ 6p^2$$

$$Br \text{ —— } (KLM)\ 4s^2\ 4p^5$$

Out of the different electrons, the $6s^2$ $6p^2$ electrons of lead and $4s^2$ $4p^5$ electrons of bromine represent the outer electrons of the PbBr molecule.

Following Mulliken's[12] notation, the lowest electronic configuration of the PbBr molecule may be written as

$$(KLLMMNO_{spd})\ (z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4v\pi - (^2\pi_r)\ldots(1)$$

This configuration has been identified to represent the ground state of the different monohalides of silicon, tin

and load studied so far. Here ($z\sigma$) represents the bonding orbital of the type ($6s\,\sigma_{Pb} + 4s\,\sigma_{Br}$, σ) and ($y\sigma$) represents the antibonding orbital of the type ($6s\,\sigma_{Pb} - 4s\,\sigma_{Br}$, σ); ($\omega\pi$) and ($v\pi$) represent bonding and antibonding orbitals of the type ($6p\,\pi_{Pb} + 4p\,\pi_{Br}$, π) and ($6p\,\pi_{Pb} - 4p\,\pi_{Br}$, π); ($x\sigma$) represents a bonding orbital of the type ($6p\,\sigma_{Pb} + 4p\,\sigma_{Br}$, σ). This configuration gives the electronic term $^2\pi_r$, which is therefore the ground state of the molecule.

The first excited state observed for the fourth group halides by different workers are as follows:

For the visible band system of the SnCl and SnBr molecules Sarma[13] has mentioned that the electronic transition involved probably is of the $^2\Sigma$-$^2\Sigma$ type on the ground that the rotational structure is relatively more open as compared to the ultraviolet systems.

From a revised rotational analysis of the (0, 0) band of the A-X system of the SiF molecule, Johns and Barrow[14] have suggested that the transition is $^2\Sigma$-$^2\pi$ case (a) and have observed eleven of the twelve branches predicted for this transition. The electronic configuration suggested by them for the state A is

$$\text{---} \quad (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)(v\pi)^2 \; ^2\Sigma^+ \quad \ldots..(2)$$

Later Barrow, Butler, Johns and Powell[15] summarised the results on the spectra of SiF, GeF, SnF and PbF molecules and mentioned that a more probable configuration for the first excited state of all these molecules is

$$\cdots\cdots(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2(u\sigma) \quad {}^2\Sigma^+ \quad \ldots.(3)$$

where $(u\sigma)$ is antibonding.

Barrow, Kopp and Morer[16] have given the configuration (3) for the state A (ν_0 = 20136.6 cm^{-1}) in SnF molecule. The antibonding nature of the $(u\sigma)$ orbital has been supported by the observed fact that the vibrational frequency in the state A is considerably smaller than that in the ground state and the internuclear distance is larger.

While discussing the electronic transition of the 3300 Å band system of the SiF molecule, Verma[17] has also supported the probability of the configuration (3) for the A $^2\Sigma^+$ state. He has further indicated that the $(v\pi)$ and $(x\sigma)$ electrons in SiF are almost nonbonding or have the same bonding character, ruling out the possibility of the configuration (2).

The state A was identified as the $^2\Sigma^+$ state of the configuration (3) by K.M.Rao and Rao[6] in PbF and by

V.S.Rao and Rao[7] in PbCl molecules. For the PbCl molecule V.S.Rao and Rao[7] have suggested that the A-X system arises from a $\frac{1}{2} - \frac{1}{2}$ transition of case (c) type on the basis of the observation that only two branches appear. In the light of the facts that the molecule PbBr is very heavy and only single P and R branches appear we may assume that the Hund's case (c) applies for the ground and the first excited states and the transition of the present system is a case (c) ($\frac{1}{2} - \frac{1}{2}$), given by the following configuration:

$$(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2(u\sigma) - {}^2\Sigma^+(\tfrac{1}{2})$$

$$- (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2(v\pi) - {}^2\pi_{\frac{1}{2}}(\tfrac{1}{2})$$

where $(v\pi)$ has now been taken as the nonbonding orbital and $(u\sigma)$ as the antibonding one.

REFERENCES

1. Barratt, S. — Trans.Farad.Soc.25, 750 (1929).
2. Howell, H.G. and Rochester, G.D. — Proc.Univ.Durham Phil.Soc.Ser.A, 9, 126 (1934).
3. Morgan, F. — Phys.Rev. 49, 47 (1936).
4. Rochester, G.D. — Proc.Roy.Soc.167A, 367 (1938).
5. Wieland, K. and Newborgh, R. — Helv.Phys.Acta, 25, 87 (1952).
6. Rao, K.M. and Rao, P.T. — Can.J.Phys. 42, 690 (1964).
7. Rao, V.S. and Rao, P.T. — Z.Physik 181, 53 (1964).
8. Harrison, G.R. — M.I.T.Wavelength Tables, John Wiley: New York (1939).
9. "Table of Wave-numbers" — N.B.S.Monograph No.3, Vol.1 (1960).
10. Lal, K.M. and Khanna, B.N. — Can.J.Phys. 45, 3663 (1967).
11. Herzberg, G. — Spectra of Diatomic Molecules, D.Van Nostrand:Princeton, (1950).
12. Mulliken, R.S. — Rev.Mod.Phys. 4, 1 (1932).
13. Sarma, P.R.K. — J.Mol.Spectr. 17, 252 (1965).
14. Johns, J.W.C. and Barrow, R.F. — Proc.Phys.Soc.(Lond.) 71, 476 (1958)
15. Barrow, R.F., Butler, D., Johns, J.W.C. and Powell, J.L. — Proc.Phys.Soc.(Lond.) 73, 317 (1959)

16. Barrow, R.F., Kopp, I. and Moror, A.J. — Proc.Phys.Soc. (Lond.) 79, 749 (1962).

17. Verma, R.D. — Can.J.Phys. 40, 986 (1962).

CHAPTER II

Rotational Analysis of the Visible Band System of the $BiBr$ Molecule.

ABSTRACT

The rotational structure of the visible band system (4600 Å - 6350 Å) of the BiBr molecule has been recorded in the second order of a 35 ft concave grating spectrograph (30,000 lines/inch) with a reciprocal dispersion of 0.32 Å/mm. The structure due to two isotopes of bromine has been resolved. A rotational analysis of (7, 0), (8, 0), (9, 0), (10, 1), (1, 4), (0, 6) and (0, 7) bands of this system has been carried out leading to the determination of the following rotational constants:

		$Bi^{79}Br$	$Bi^{81}Br$
B_0'	(cm^{-1})	0.0364_2	0.0359_2
B_0''	(cm^{-1})	0.0436_7	0.0428_7
r_0'	(Å)	2.84_2	2.84
r_0''	(Å)	2.59_6	2.59_6

$\alpha_e' = 0.00025\ cm^{-1}$; $\alpha_e'' = 0.00015\ cm^{-1}$

As the structure shows the presence of only P and R branches, the system appears to be similar to the visible band system of the BiCl molecule and a $0^+ - 0^+$ transition has been suggested.

INTRODUCTION

The spectra of the diatomic halides of bismuth has been widely studied though it is the heaviest atom in the Vth group of the periodic table. As early as in 1934, Howell and Rochester[1] observed the visible band system of the BiBr molecule in emission using a high frequency discharge. Morgan[2] recorded two systems in absorption, one in the region 3860 Å - 4130 Å (B system) and the other in the region 4590 Å - 5438 Å (A system), by passing bromine vapour over molten mass of bismuth placed in an open iron tube at 900°C inside a furnace. He attributed both these systems to the BiBr molecule and made the vibrational analyses. Sur and Majumdar[3] obtained in absorption three other systems lying in the regions 2709 Å - 2963 Å, 2336 Å - 2450 Å and 2200 Å - 2350 Å and designated them as C, D and E respectively, naming the two longer wavelength systems as A and B. Sankarnarayanan, Patel and Narayanan[4] recorded the "A" system of the BiBr molecule in emission using a transformer discharge and gave a detailed vibrational analysis of nearly 200 bands lying in the region 4590 Å - 6063 Å. They also measured the isotopic shift due to bromine isotopes in a number of bands. The "A" system of the BiBr molecule seems to be analogous to the red degraded A-X

system of the BiCl molecule. Khanna[5] reported the rotational analysis of the A-X system of the BiCl molecule and he observed only two branches, one P and one R. The transition was concluded to be $0^+ - 0^+$, a case (c) equivalent of $^3\pi - {}^3\Sigma^-$.

Since bismuth has got no isotopes and bromine has only two isotopes of equal abundance, it was felt that possibly the structure of the bands of the visible system of this molecule could also be resolved. The bands which are free from any serious overlapping, namely (7, 0), (8, 0),(9, 0), (10, 1), (4, 1), (1, 4), (0, 6) and (0, 7) were chosen and recorded in the second order of a 35 ft concave grating spectrograph (30,000 lines/inch) at a reciprocal dispersion of 0.32 Å/mm. The rotational analysis of all the bands has been carried out and the constants for the $Bi^{79}Br$ and $Bi^{81}Br$ molecules have been obtained. Most of the bands show the presence of only two series of lines of almost equal intensity. The rotational lines belonging to the two isotopic molecules have been sorted out and are given in separate tables. The results described in this chapter indicate that the present system is similar to the A-X system of the BiCl molecule. The electronic transition involved in the system is also discussed.

While finalising the data, we came across a note by Murty and Rao[6]. They have studied the structure of three bands (1, 4), (7, 4) and (7, 0) of this system from a record taken in the first order of a 21 ft grating spectrograph (dispersion 1.25 Å/mm) and have reported that each band reveals a simple structure consisting of single P and R branches. In the present investigation, with a dispersion of 0.32 Å/mm and a theoretical resolution of 3,60,000, the P and R branches could not be resolved except in the case of (7, 0) band (Fig.1) and that too at about J = 95 for the R branch, resulting in a four line structure onwards. The structure of all the other bands contains only two series of lines upto the tail of the bands. Probably Murty and Rao[6] have taken the two series of lines in the (7, 0) band as the P and R branches of $Bi^{79}Br$ molecule while saying nothing regarding the lines of the equally abundant $Bi^{81}Br$ species. They have not given any spectrogram or wavenumbers of the lines of bands and as such it is difficult to say whether they have taken the P and R branches as resolved or overlapped. Presently, the two series of lines have been assigned as arising due to two equally intense band heads of $Bi^{79}Br$ and $Bi^{81}Br$ species and therefore the P and R branches are taken as overlapped for all the bands except for the (7, 0) band.

EXPERIMENTAL DETAILS

The bismuth monobromide molecule was excited with the help of a 2450 Mc/sec microwave generator in an U shaped pyrex tube 5 mm in diameter closed at one end and held vertically. The open limb was connected to a rotary pump and was continuously pumped. The microtherm antenna was placed at the mid point of the closed limb, 2 cm in length, and an intense glow greenish blue in colour of one cm in length was obtained. This source was found to be more appropriate for excitation of the bands lying in the shorter wavelength region of the system as compared to the transformer discharge. A pure sample of bismuth tribromide (B.D.H.) was used. The preliminary investigation was made in the first and second orders of a 21 ft concave grating spectrograph (15,000 lines/inch) at this laboratory. The Ilford photographic plates HP3 were used and the time of exposure required ranged from one to three hours. The final spectrum was recorded at the Department of Spectroscopy, B.H.U., Varanasi, in the second order of a 35 ft concave grating spectrograph (30,000 lines/ inch, ruled width 6 inches) having a reciprocal dispersion of 0.32 Å/mm and blazed at 7500 Å in the first order. All the bands lying in the region 4600 Å - 5900 Å were recorded but only eight bands (7, 0), (8, 0), (9, 0), (10, 1)

(4, 1), (1, 4), (0, 6) and (0, 7) are free from any serious overlapping and therefore chosen for the rotational analyses. The exposure time ranged from 3 to 6 hours for bands lying in the region 4600 Å - 4750 Å recorded on ORWO Blau Rapid plates and 8 to 10 hours for bands lying in the region 9100 Å - 9350 Å recorded on Ilford HP3 plates. The measurements were made with the help of Carl Zeiss Abbe comparator against iron lines as the comparison spectrum using as standards the wavelengths given by Harrison[7] (M.I.T.Tables). The relative accuracy in our measurements is of the order of ± 0.04 cm^{-1} for sharp lines and ± 0.10 cm^{-1} for broad diffuse lines. The Table of wavenumbers (N.B.S., United States[8]) was used for conversion to wavenumbers in vacuo.

EXPERIMENTAL DATA AND ROTATIONAL ANALYSIS

All the bands of this system are red degraded and show two heads of equal intensity. The vibrational assignments given by Sankaranarayanan and others[4], are substantiated by the observed isotopic shifts for most of the bands. Taking this system as analogous to the A-X system of the BiCl molecule, one would expect mainly one P and one R branch for each of the two isotopic heads resulting in a four branch structure for each band. Enlargements

of the spectra of — the (7,0), (0,6), (1,4) and (8,0) bands are given in Figs.1 to 4.

In case of heavy molecules the Franck-Condon parabola for the transition between the ground state and the first excited state is generally very wide which is also the case with the band system under discussion. This results in a large difference in the B values of the lower and the upper states leading to a small separation between the band origin and the band head. The origin to head separation for A-X system has been found to be very small (~ 1 cm^{-1}) for PbCl by Rao and Rao[9], for PbBr by Lal and Khanna[10] and for BiCl by Khanna[5]. A small origin to head separation leads to a small difference in the J numbering of the P and R lines falling at one place and gives rise to the following two facts:

(i) The P and R branches overlap each other over a large portion of the band at moderate resolutions and get resolved only at high J values;

(ii) After they are resolved, the two branches cross each other a few times only and the number of crossing goes on decreasing as we move from lighter to heavier molecules.

These facts are a conclusion drawn after looking at the observed rotational structure of heavy molecules e.g. lead and bismuth halides. On looking at the structure of the (0, 6) band(Fig.2)one finds two series of lines of

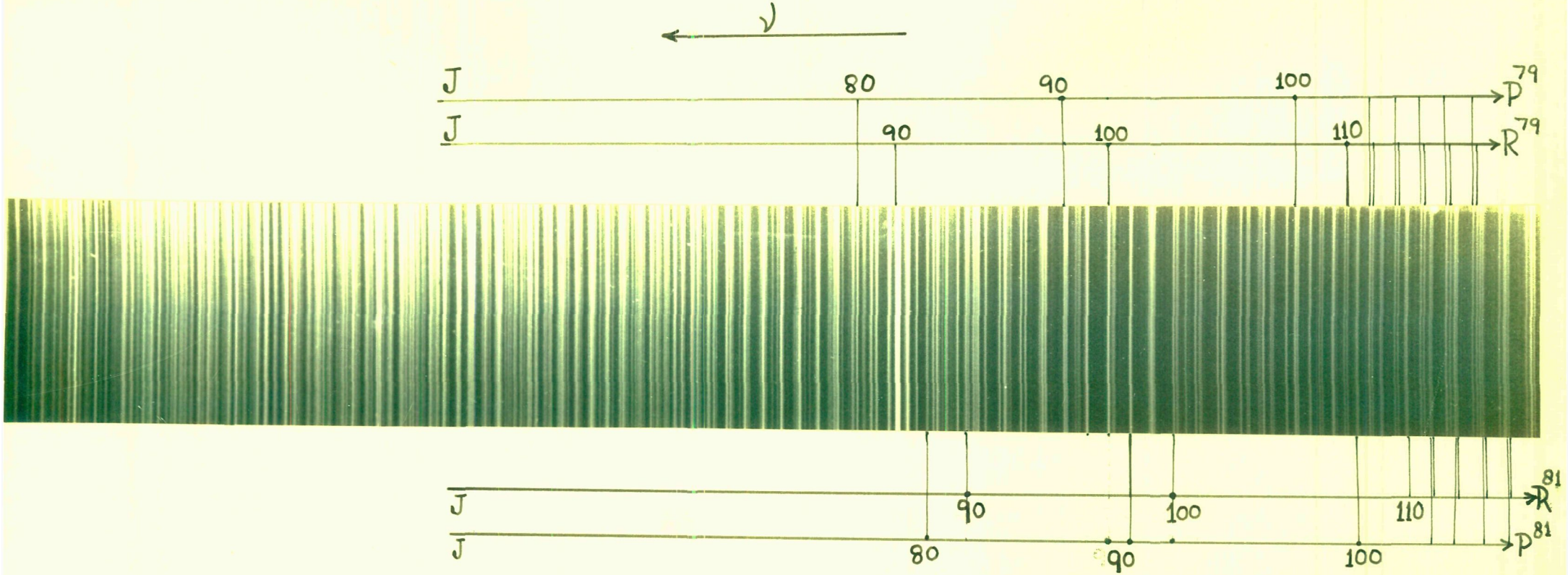

Fig. 1. The Enlargement of the (7, 0) band of the (4600-6350 Å) System of BiBr (35 ft grating II order).

almost equal intensity throughout the band spread. The two branches cross each other very frequently and the total number of crossing is more than eight. Therefore, the experimental observations mentioned earlier led us to believe that the two series of lines are not the P and R branches of one isotopic head. Moreover, we are unable to pick out any branches which may be assigned to the other equally intense isotopic head lying at 11 cm^{-1} apart; once we say that the two series of observed lines are the P and R branches belonging to one of the heads. Consequently, the explanation chosen is that the one series of lines belong to $Bi^{81}Br$ head (nearer one) and the other series of lines to $Bi^{79}Br$ head. The P and R branches of either species are considered as overlapped throughout the band. The large number of crossing is also explained by the large vibrational isotopic shift ($\nu - \nu^i = -11\ cm^{-1}$) where ν^i corresponds to the $Bi^{81}Br$ species. This explanation is further supported by the structure of the (7, 0) band (Fig.1)for which the isotopic shift is small ($\nu - \nu^i = +5\ cm^{-1}$) and the number of crossing is also comparatively smaller. In the middle portion of the (7, 0) band two series of lines of equal intensities are observed, each of which splits further into two at about R(105), giving rise to a four line structure near the band tail. These four

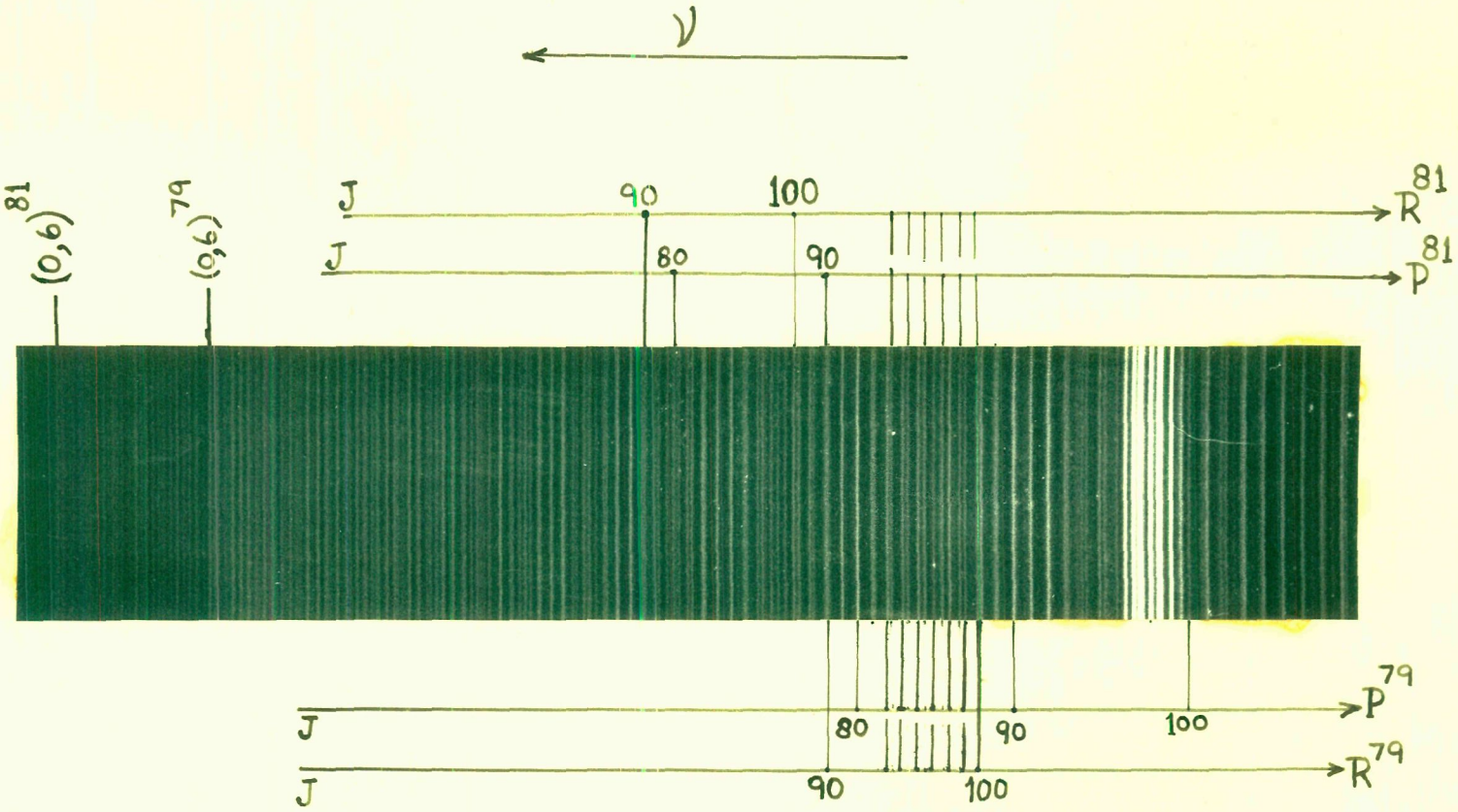

Fig. 2. The Enlargement of the (0, 6) band of the (4600-6350 Å) System of BiBr (35 ft grating I order).

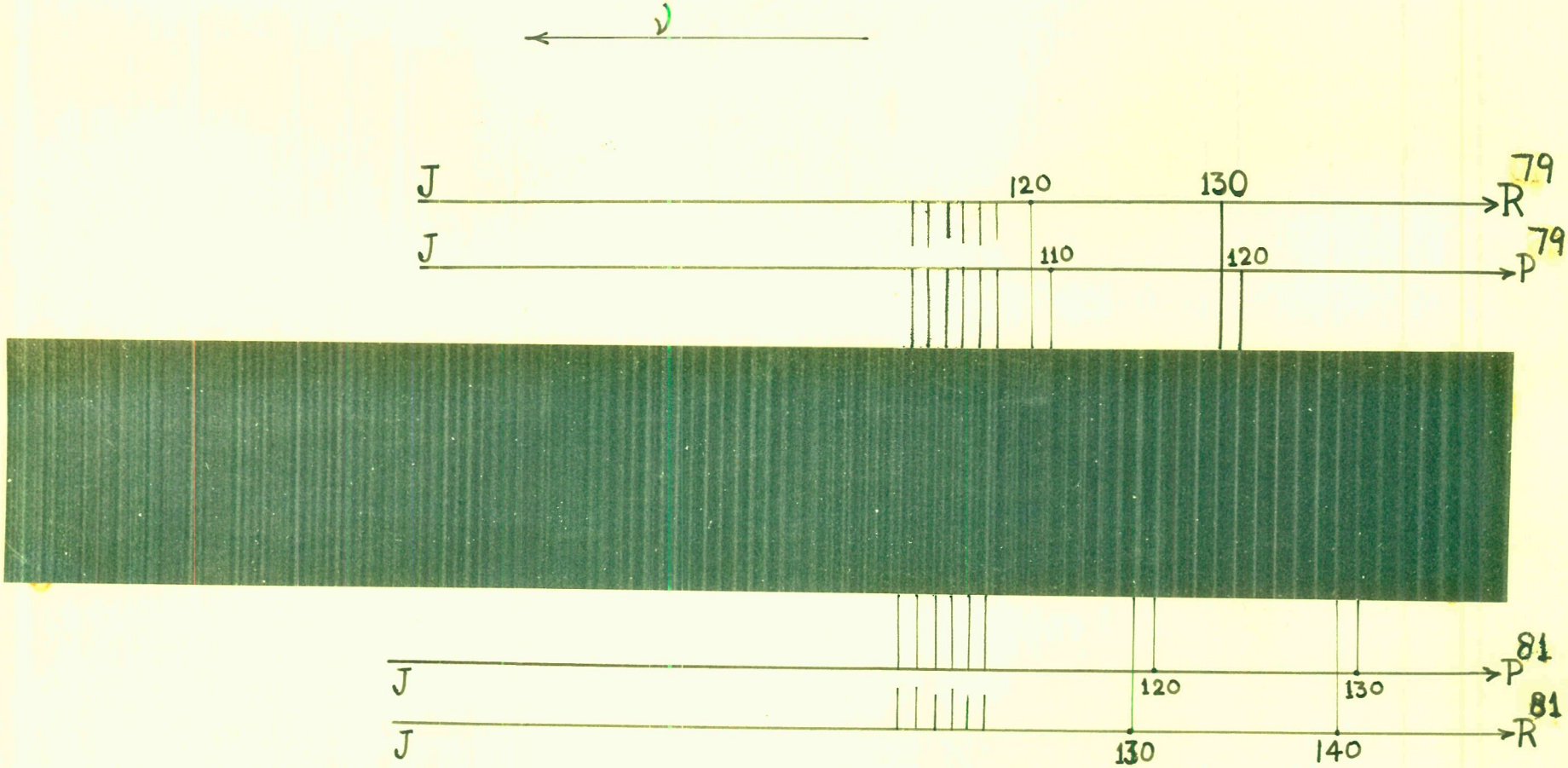

Fig. 3. The Enlargement of the (1, 4) band of the (4600-6350 Å) System of BiBr (35 ft grating I order).

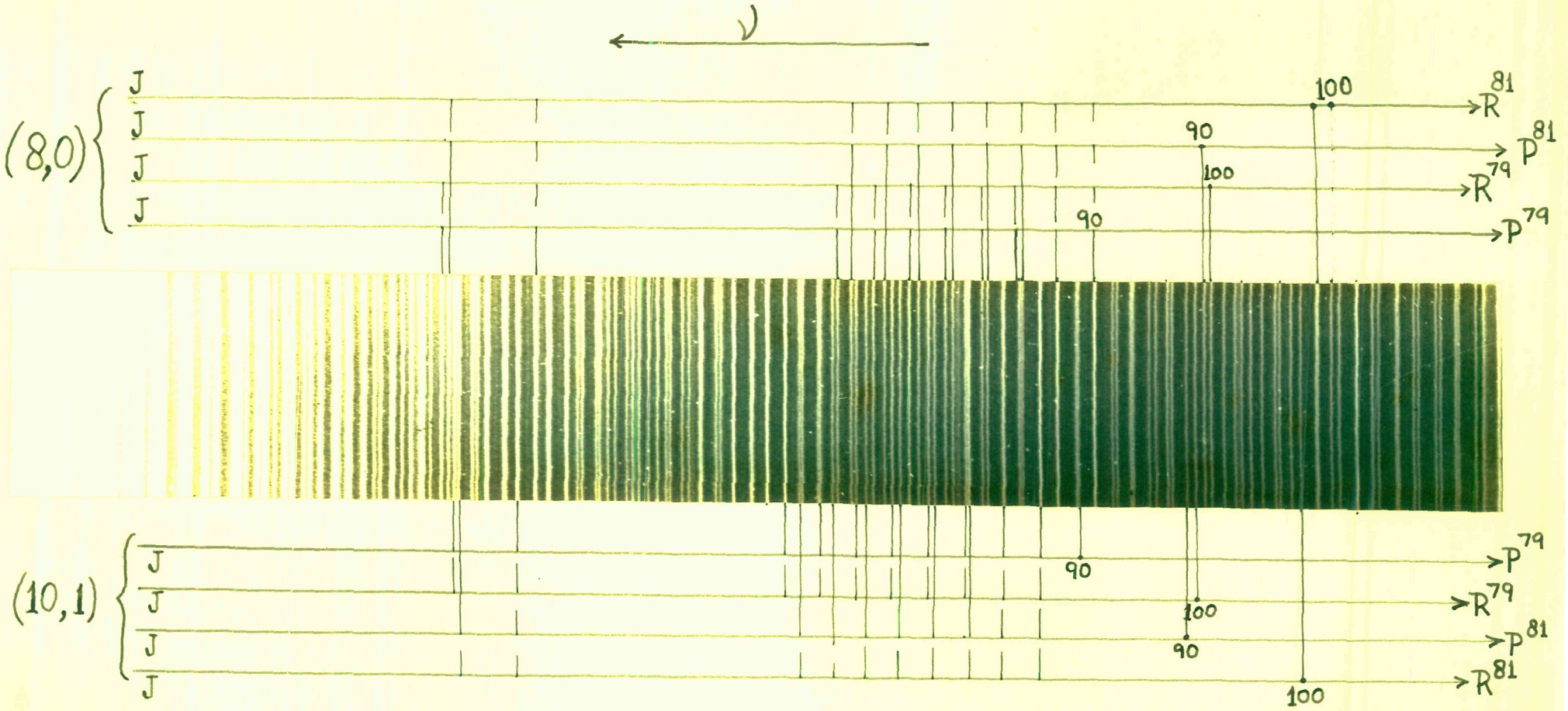

Fig. 4. The Enlargement of the (8, 0) and (10, 1) bands of the (4600-6350 Å) System of BiBr (35 ft gratin
II order)

series of lines are marked as ^{79}R, ^{79}P, ^{81}R and ^{81}P in Fig.1. The single series of lines that first gets resolved into two belong to the shorter wavelength head ($Bi^{79}Br$) and the other series that gets resolved later belongs to longer wavelength head ($Bi^{81}Br$). Thus atleast in the case of (7, 0) band the expected four branches have been resolved. In the case of (8, 0)(Fig.4) and (9, 0) bands the four branches are not resolved because their band width is left smaller due to the overlapping of other bands as compared to (7, 0) band. Similar is the case with the (0, 6), (1, 4) and (10, 1) bands (Figs.2, 3, 4). The heads of the (8, 0) and (10, 1) bands are very near to each other and their structure is overlapping (Fig.4). Sorting out of the branches in this case did not create any difficulty as the structure is resolved fairly well.

The vacuum wavenumbers and the rotational assignments of the individual lines of all the bands belonging to $Bi^{79}Br$ are given in tables I and II, whereas the tables III and IV contain the assignments for the lines belonging to $Bi^{81}Br$ molecule.

The absolute J numbering of the rotational lines has been fixed from the $\Delta_2F(J)$ versus J curves (Fig 5 to 8) and the rotational constants were determined following the usual

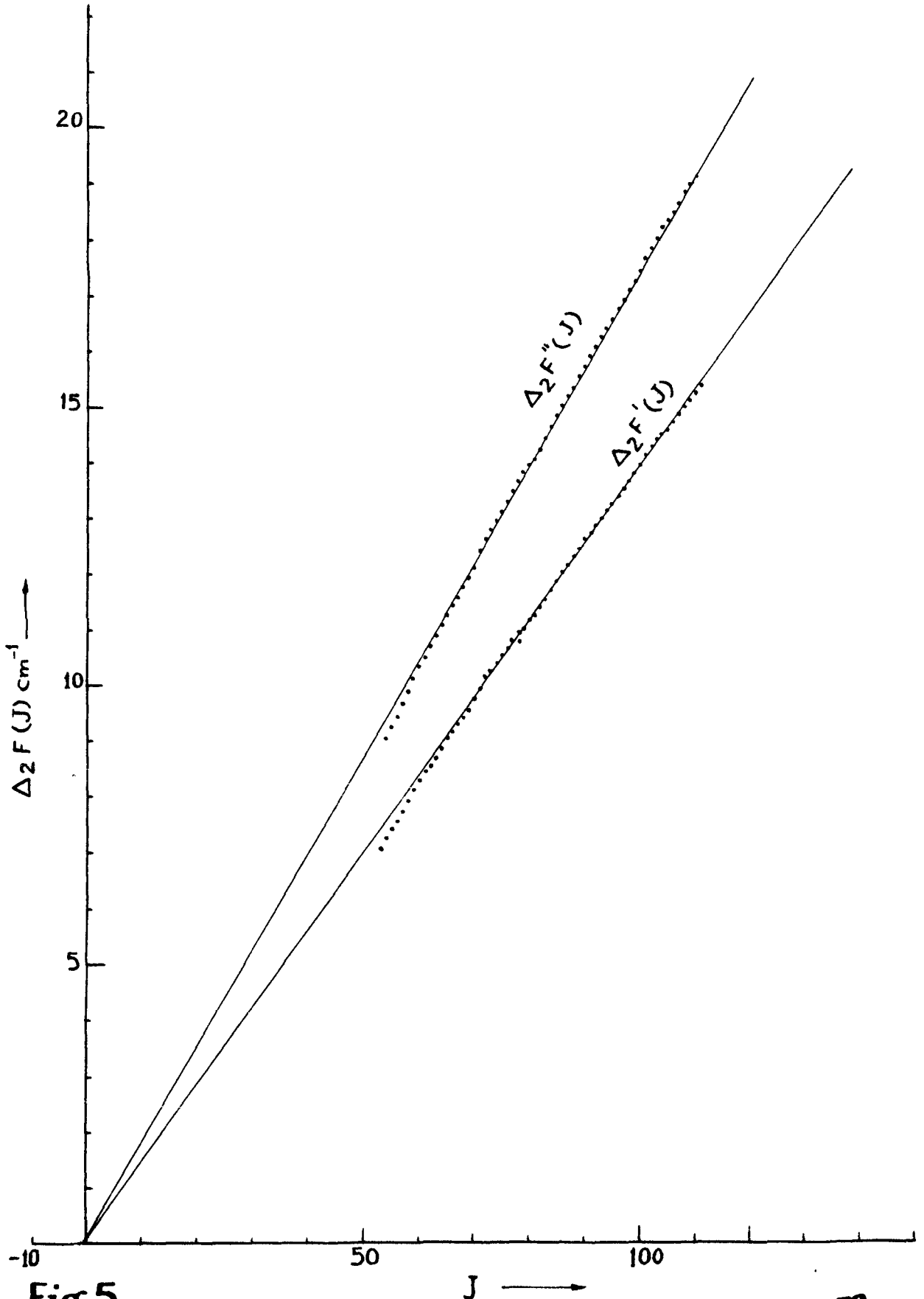

Fig. 5 $\Delta_2 F(J)$ Vs. J CURVES FOR THE $(7,0)^{79}$ BAND

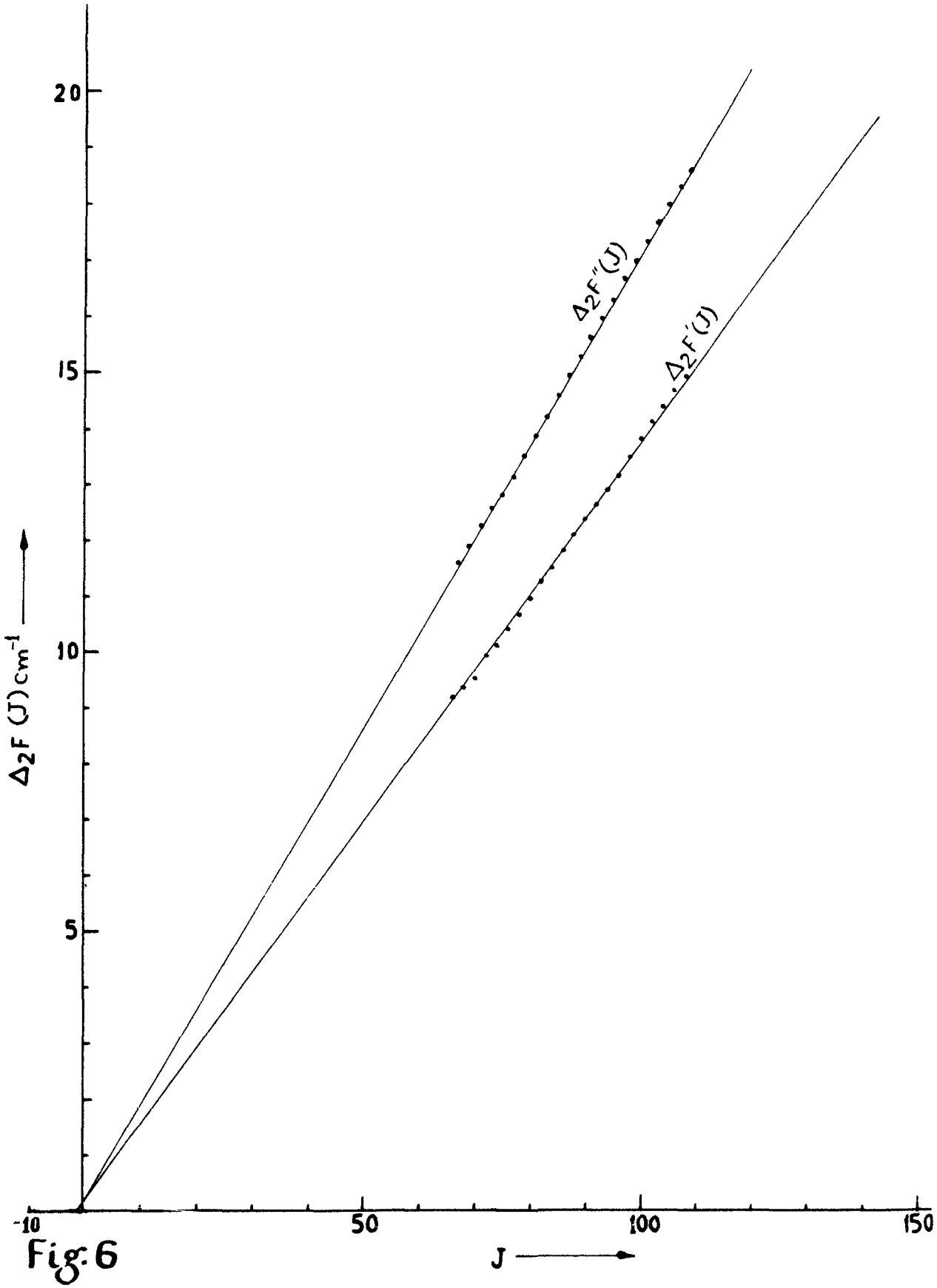

Fig: 6

$\Delta_2 F(J)$ Vs. J CURVES FOR THE $(7,0)^{81}$ BAND

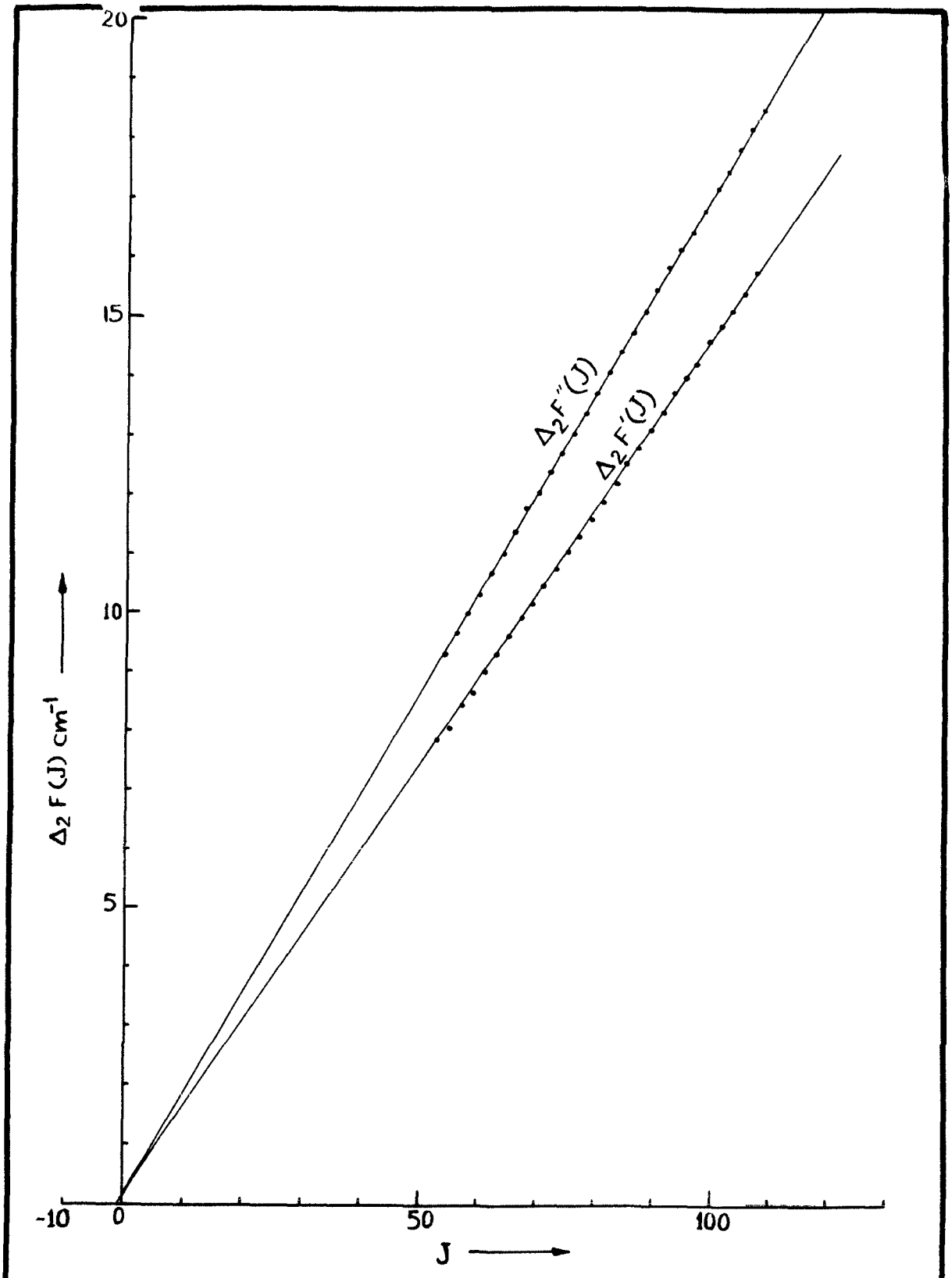

Fig. 7

$\Delta_2 F(J)$ Vs. J CURVES FOR THE $(0,6)^{79}$ BAND

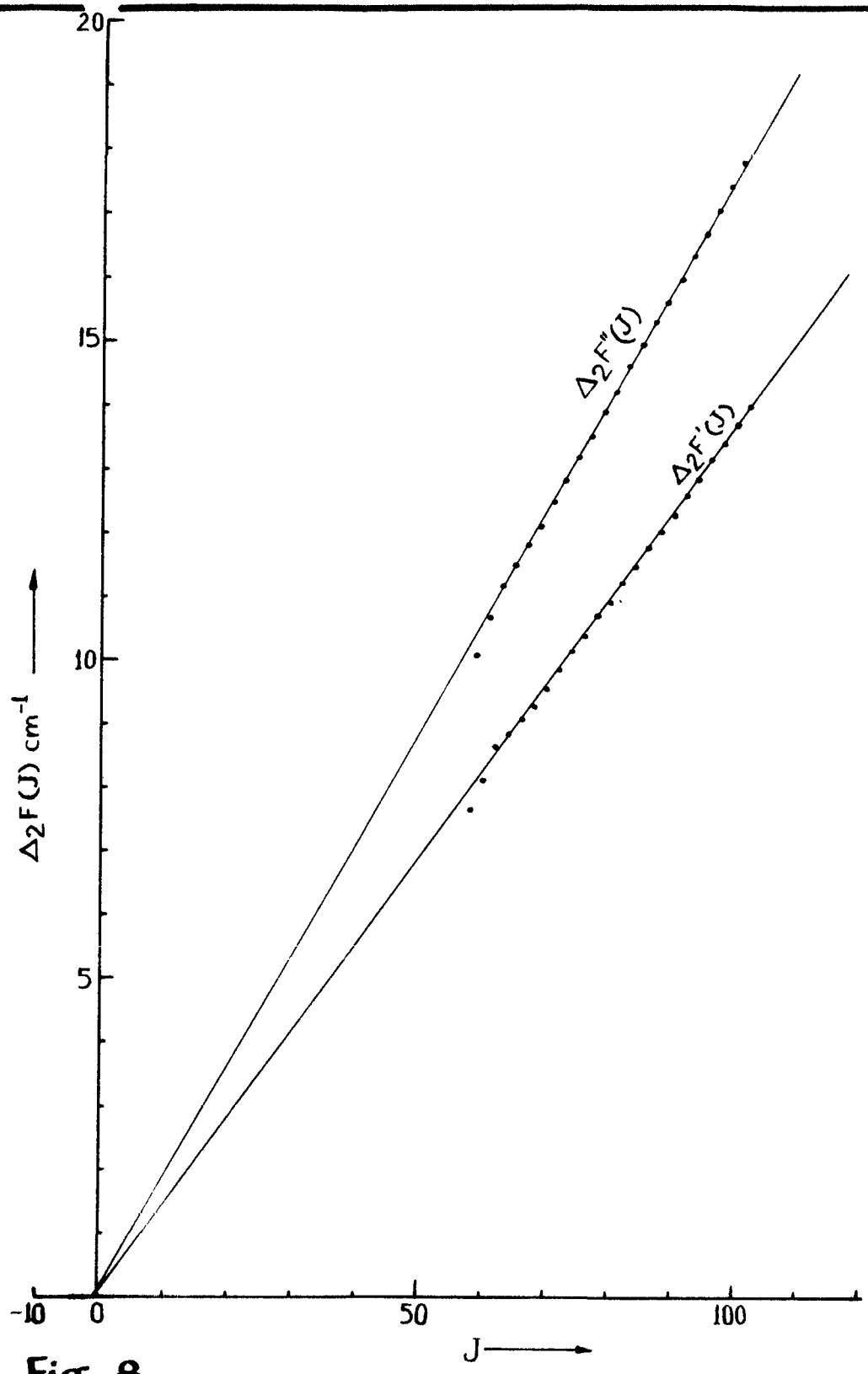

Fig. 8

$\Delta_2 F(J)$ Vs. J CURVES FOR THE $(10,1)^{79}$ BAND

TABLE I. Vacuum Wavenumbers and Rotational Assignments for (7, 0), (8, 0), (9, 0) and (10, 1) bands of $DI^{79}Br$ molecule.

J	7 - 0		8 - 0		9 - 0		10 - 1	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
45		21348.81						
46		48.00						
47		47.16						
48		46.30						
49		45.43						
50		44.53						21447.05
51		43.63						46.13
52		42.70						45.16
53	21348.81	41.75						44.16
54	48.00	40.75						43.19
55	47.16	39.75						42.08
56	46.30	38.73						40.89
57	45.43	37.69					21447.05	39.69
58	44.53	36.60					46.13	38.50
59	43.63	35.51	-	21436.47	-	21543.56	45.16	37.25
60	42.70	34.41	-	35.23	-	42.34	44.16	36.01

TABLE I (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
61	21341.75	21333.28		21433.99		21541.14	21443.19	21434.72
62	40.75	32.20		32.66		39.77	42.08	33.44
63	39.75	31.04		31.42		38.44	40.89	32.20
64	38.73	29.86		30.04		37.15	39.69	30.87
65	37.69	28.66		28.71		35.82	38.50	29.54
66	36.60	27.45	21436.47	27.38	21543.56	34.48	37.25	28.20
67	35.51	26.23	35.23	26.04	42.34	33.09	36.01	26.83
68	34.41	25.00	33.99	24.62	41.14	31.75	34.72	25.45
69	33.28	23.72	32.66	23.20	39.77	30.27	33.44	23.98
70	32.20	22.45	31.42	21.77	38.44	28.84	32.20	22.65
71	31.04	21.09	30.04	20.31	37.15	27.45	30.87	21.18
72	29.86	19.73	28.71	18.84	35.82	25.97	29.54	19.71
73	28.66	18.40	27.38	17.37	34.48	24.49	28.20	18.15
74	27.45	17.06	26.04	15.85	33.09	23.00	26.83	16.73
75	26.23	15.68	24.62	14.39	31.75	21.48	25.45	15.17
76	25.00	14.33	23.20	12.78	30.27	19.90	23.98	13.65
77	23.72	12.93	21.77	11.22	28.84	18.37	22.65	12.05
78	22.45	11.51	20.31	09.66	27.45	16.84	21.18	10.49

TABLE I (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
79	21321.09	21310.04	21418.84	21408.01	21525.97	21515.27	21419.71	21408.88
80	19.73	08.60	17.37	06.41	24.49	13.60	18.15	07.28
81	18.40	07.16	15.85	04.80	23.00	11.98	16.73	05.58
82	17.06	05.68	14.39	03.16	21.48	10.32	15.17	03.98
83	15.68	04.14	12.78	01.46	19.90	08.56	13.65	02.28
84	14.33	02.62	11.22	21399.77	18.37	06.97	12.05	00.59
85	12.93	01.06	09.66	98.07	16.84	05.29	10.49	21398.89
86	11.51	21299.49	08.01	96.33	15.27	03.62	08.88	97.11
87	10.04	97.21	06.41	94.54	13.60	01.82	07.28	95.37
88	08.60	96.31	04.80	92.80	11.98	00.08	05.58	93.58
89	07.16	94.69	03.16	90.97	10.32	21498.26	03.98	91.80
90	05.68	93.06	01.46	89.23	08.56	96.40	02.28	90.01
91	04.14	91.40	21399.77	87.40	06.97	94.65	00.59	88.18
92	02.62	89.75	98.07	85.57	05.29	92.84	21398.89	86.31
93	01.06	88.07	96.33	83.70	03.62	91.02	97.11	84.43
94	21299.49	86.37	94.54	81.78	01.82	89.07	95.37	82.56
95	97.91	84.65	92.80	79.90	00.08	-	93.50	80.63
96	96.31	82.92	90.97	77.98	21498.26		91.80	78.67

TABLE I (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
97	21294.69	21281.17	21389.23	21376.02	21496.40	-	21390.01	21376.75
98	93.06	79.40	87.40	-	94.65		88.18	74.78
99	91.40	77.60	85.57		92.84		86.31	72.77
100	89.75	75.78	83.70		91.02		84.43	70.76
101	88.07	73.95	81.78		89.07		82.56	68.71
102	86.37	72.09	79.90		-		80.63	66.70
103	84.65	70.23	77.98				78.67	
104	82.85	68.34	76.02				76.75	
105	81.02	66.43	-				74.78	
106	79.24	64.52					72.77	
107	77.43	62.55					70.76	
108	75.57	60.58					68.71	
109	73.73	58.61					66.70	
110	71.80	56.62					-	
111	70.01	54.60						
112	68.08	-						
113	66.16							
114	64.22							
115	62.26							

TABLE II. Vacuum wavenumbers and Rotational Assignments for (0, 6), (0, 7) and (1, 4) bands of $Bi^{79}Br$ Molecule.

J	0 - 6		0 - 7		1 - 4	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
41		19243.73				
42		43.06				
43		42.47				
44		41.80				
45		41.29				
46		40.62				
47		39.95				
48		39.32				
49		38.66				
50		38.03				
51		37.25				
52		36.55				
53	19243.73	35.88				
54	43.06	35.10	—	—	—	—
55	42.47	34.44	—	—	—	—

TABLE II (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
56	19241.60	19233.59				19777.11
57	41.29	32.81				76.21
58	40.62	32.07				75.35
59	39.95	31.29				74.45
60	39.32	30.44				73.71
61	38.66	29.66				72.93
62	38.03	28.89				71.99
63	37.25	27.96				71.13
64	36.55	27.15				70.11
65	35.80	26.26				69.21
66	35.10	25.37				68.27
67	34.44	24.49			19777.11	67.41
68	33.39	23.56			76.21	66.51
69	32.81	22.64			75.35	65.35
70	32.07	21.75			74.45	64.48
71	31.29	20.79	—	—	73.71	63.47
72	30.44	19.83	—	—	72.92	62.45

TABLE II (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
73	19229.66	19218.91			19771.99	19761.40
74	28.89	17.95			71.13	60.54
75	27.96	16.95		19004.34	70.11	59.40
76	27.15	15.99		03.15	69.21	58.31
77	26.26	14.95		01.99	68.27	57.26
78	25.37	13.96		00.77	67.41	56.36
79	24.49	12.89		18999.50	66.51	55.23
80	23.56	11.78		98.40	65.51	54.09
81	22.64	10.78		97.28	64.48	52.92
82	21.75	09.67		95.93	63.47	51.67
83	20.79	08.60		94.67	62.45	50.66
84	19.83	07.46		93.64	61.40	49.37
85	18.91	06.39		92.68	60.54	48.20
86	17.95	05.32	19004.34	91.65	59.40	47.07
87	16.95	04.18	03.15	90.59	58.31	45.90
88	15.99	03.00	01.99	89.29	57.26	44.69
89	14.95	01.85	00.77	87.85	56.36	43.48

TABLE II (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
90	19213.96	19200.71	18999.50	18986.55	19755.23	19742.16
91	12.89	19199.49	98.40	85.25	54.09	40.79
92	11.78	98.28	97.28	83.93	52.92	39.58
93	10.78	97.06	95.93	82.69	51.67	38.41
94	09.67	95.88	94.67	81.18	50.66	37.09
95	08.60	94.63	93.64	80.02	49.37	35.76
96	07.46	93.37	92.68	78.73	48.20	34.56
97	06.39	92.19	91.65	77.65	47.07	33.15
98	05.32	90.92	90.59	76.31	45.90	31.83
99	04.18	89.58	89.29	74.91	44.69	30.39
100	03.00	88.29	87.85	73.32	43.03	29.07
101	01.85	87.00	86.55	71.88	42.16	27.66
102	00.71	85.68	85.25	70.48	40.79	26.34
103	19199.49	84.39	83.93	68.93	39.58	24.86
104	98.28	83.08	82.69	67.49	38.41	23.50
105	97.06	81.66	81.18	65.98	37.09	21.98
106	95.88	80.23	80.02	64.65	35.76	20.54

TABLE II (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
107	19194.63	19178.87	18978.73	18963.25	19734.56	19719.10
108	93.37	77.62	77.75	61.74	33.15	17.66
109	92.19	76.14	76.31	60.26	31.83	16.19
110	90.92	74.93	74.91	58.86	30.39	14.59
111	89.58	73.61	73.32	57.24	29.07	13.12
112	88.29	72.28	71.88	55.77	27.66	11.56
113	87.00	-	70.48	54.22	26.34	10.05
114	85.68		68.93	52.68	24.86	08.53
115	84.39		67.49	51.10	23.50	06.90
116	83.03		65.92	49.48	21.98	05.27
117	81.66		64.69	47.94	20.54	03.75
118	80.23		63.25	46.36	19.10	02.16
119	78.87		61.74	44.71	17.66	00.53
120	77.62		60.26	43.02	16.19	19698.86
121	76.14		58.86	41.37	14.59	97.15
122	74.93		57.24	39.75	13.12	95.48
123	73.61		55.77	38.10	11.56	93.78

TABLE II (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
124	19172.28	-	18954.22	18936.38	19710.05	19692.11
125	-	-	52.68	34.73	08.53	90.32
126			51.10	33.01	06.90	89.62
127			49.48	31.29	05.27	86.91
128			47.94	29.53	03.75	85.17
129			46.36	27.81	02.16	83.35
130			44.71	26.06	00.53	81.60
131			43.02	24.34	19699.85	79.86
132			41.37	22.53	97.15	78.00
133			39.75	20.68	95.48	76.26
134			38.10	18.89	93.78	74.36
135			36.38	17.07	92.11	72.62
136			34.73	15.24	90.32	70.88
137			33.01	13.33	88.62	69.06
138			31.29	11.52	86.91	-
139			29.53	09.66	85.17	
140			27.81	-	83.35	

TABLE III. Vacuum wavenumbers and Rotational Assignments for (7, 0), (8, 0), (9, 0) and (10, 1) bands of $Bi^{81}Br$ molecule.

J	7 - 0		8 - 0		9 - 0		10 - 1	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
54						21542.83		21436.99
55						41.64		35.81
56				21433.66		40.43		34.60
57		21331.96		32.50		39.23		33.40
58		30.96		31.32		38.02		32.23
59		29.86		30.12		36.77		31.05
60		28.68		28.92		35.62	21430.15	29.81
61		27.55		27.69	21542.33	34.41	36.99	28.57
62		26.59		26.40	41.60	33.16	35.81	27.38
63		25.40	21433.66	25.22	40.43	31.86	34.60	26.04
64		24.25	32.50	23.98	39.23	30.56	33.40	24.80
65	21331.96	22.95	31.32	22.65	38.02	29.22	32.23	23.55
66	30.96	21.70	30.12	21.32	36.77	27.92	31.05	22.19
67	29.86	20.50	28.92	19.98	35.62	26.62	29.81	20.86
68	28.68	19.36	27.69	18.61	34.41	25.23	28.57	19.48
69	27.55	18.13	26.40	17.23	33.16	23.93	27.38	18.17

TABLE III (Continued)

J		R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
70	2	21326.59	21316.88	21425.22	21415.69	21531.86	21522.58	21426.04	21416.73
71		25.40	15.58	23.98	14.39	30.56	21.15	24.80	15.30
72		24.25	14.33	22.68	12.97	29.22	19.79	23.52	13.84
73		22.95	12.97	21.32	11.54	27.92	18.37	22.19	12.41
74		21.70	11.70	19.98	10.08	26.62	16.84	20.86	10.95
75		20.58	10.36	18.61	08.56	25.23	15.27	19.48	09.43
76		19.36	09.00	17.23	07.05	23.93	13.79	18.15	07.92
77		18.13	07.55	15.88	05.58	22.58	12.31	16.73	06.41
78		16.88	06.25	14.39	03.98	21.15	10.70	15.30	04.80
79		15.58	04.84	12.97	02.38	19.71	09.16	13.84	03.29
80		14.33	03.37	11.54	00.82	18.37	07.59	12.41	01.73
81		12.97	01.90	10.08	21399.21	16.84	06.01	10.95	00.09
82		11.70	00.46	08.56	97.61	15.27	04.39	09.43	21398.48
83		10.36	21298.96	07.05	95.96	13.79	02.73	07.92	96.83
84		08.98	97.49	05.58	94.33	12.31	01.11	06.41	95.23
85		07.55	95.96	03.98	92.67	10.78	21499.40	04.80	93.50
86		06.25	94.44	02.38	90.97	09.16	97.69	03.29	91.80
87		04.84	92.66	00.82	89.23	07.59	95.98	01.73	90.10

92

TABLE III (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
88	21303.37	21291.31	21399.21	21387.54	21500.01	21494.27	21400.09	21388.36
89	01.90	89.71	97.61	95.76	04.39	92.47	21398.48	86.63
90	00.46	88.12	93.96	94.02	02.73	90.79	96.83	84.89
91	21390.96	86.52	94.33	82.24	01.11	88.91	95.23	83.06
92	97.49	84.87	92.67	80.41	21499.40	86.97	93.58	81.27
93	95.96	83.20	90.97	78.67	97.69	85.12	91.80	79.45
94	94.44	81.54	89.23	76.75	95.98	83.32	90.10	77.57
95	92.86	79.87	87.34	74.87	94.27	81.47	88.36	75.74
96	91.31	78.18	85.76	73.00	92.47	79.62	86.63	73.82
97	89.71	76.44	84.02	71.08	90.71	-	84.89	71.95
98	88.12	74.68	82.24	69.16	88.91		83.06	70.03
99	86.52	72.96	80.41	67.25	86.97		81.27	68.07
100	84.87	71.16	78.67	65.28	85.12		79.45	66.06
101	83.20	69.39	76.75	-	83.32		77.57	-
102	81.52	67.57	74.87		81.47		75.74	
103	79.85	65.75	73.00		79.62		73.82	
104	78.14	63.90	71.08		-		71.95	
105	76.41	62.04	69.16				70.03	

TABLE IV. Vacuum wavenumbers and Rotational Assignments for (0, 6), (0, 7) and (1, 4) bands of $Bi^{81}Br$ Molecule.

J	0 - 6		0 - 7		1 - 4	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
62		19241.29				
63		40.62				
64		39.97				
65		38.92				
66		38.03				
67		37.25				
68		36.40				
69		35.57				
70		34.44				
71		33.59				
72		32.81				19768.27
73		31.81				67.41
74	19241.29	30.89	—	—	—	66.51
75	40.62	29.88	—	—	—	65.51
76	39.97	28.89				64.48

TABLE IV (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
77	19238.92	19227.96				19763.47
78	38.03	26.96				62.45
79	37.25	25.93				61.40
80	36.40	24.89				60.30
81	35.47	23.90				59.17
82	34.44	22.79				58.00
83	33.50	21.75			19768.27	56.90
84	32.81	20.79			67.41	55.69
85	31.81	19.72			66.51	54.50
86	30.89	18.54		19005.64	65.51	53.30
87	29.85	17.47		04.60	64.48	52.10
88	28.89	16.37		03.48	63.47	50.84
89	27.96	15.21		02.28	62.45	49.68
90	26.96	14.07		01.99	61.40	48.47
91	25.93	12.89		18999.50	60.30	47.27
92	24.89	11.78	—	98.37	59.17	45.97
93	23.90	10.06	—	97.26	58.00	44.69

TABLE IV (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
94	19222.79	19209.38		18995.93	19756.90	19743.48
95	21.75	08.27		94.70	55.69	42.16
96	20.79	07.02		93.50	54.50	40.79
97	19.72	05.80	19003.64	91.85	53.30	39.48
98	18.54	04.55	04.60	90.31	52.10	38.18
99	17.47	03.29	03.48	89.29	50.84	36.89
100	16.36	02.04	02.28	87.85	49.68	35.53
101	15.21	19200.71	01.99	86.55	48.47	34.13
102	14.07	19199.49	18999.50	85.20	47.27	32.77
103	12.89	98.28	98.37	83.60	45.97	31.32
104	11.78	96.87	97.26	82.37	44.69	29.88
105	10.60	95.55	95.93	80.95	43.48	28.48
106	09.38	94.26	94.70	79.66	42.16	27.05
107	08.27	92.82	93.50	78.00	40.79	25.60
108	07.02	91.53	91.85	76.31	39.48	24.16
109	05.80	90.28	90.59	74.91	38.18	22.68
110	04.55	88.88	89.29	73.54	36.89	21.17

TABLE IV (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
111	19203.29	19187.33	18987.85	18972.06	19735.53	19719.63
112	02.04	86.04	86.55	70.48	34.13	18.21
113	00.71	84.57	85.20	68.93	32.77	16.65
114	19199.49	83.03	83.60	67.49	31.32	15.10
115	98.28	81.66	82.37	65.98	29.88	13.54
116	96.87	80.23	80.95	64.40	28.48	11.99
117	95.55	78.68	79.66	62.82	27.05	10.36
118	94.26	77.17	78.00	61.16	25.60	08.76
119	92.82	75.63	76.31	59.54	24.16	07.17
120	91.53	"	74.91	57.96	22.68	05.54
121	90.28		73.54	56.38	21.17	03.84
122	88.88		72.06	54.76	19.65	02.16
123	87.33		70.48	53.11	18.21	00.53
124	86.04		68.93	51.42	16.65	19698.86
125	84.57		67.49	49.73	15.10	97.15
126	83.03		65.98	48.08	13.54	95.48
127	81.66		64.40	46.36	11.99	93.78

TABLE IV (Continued)

J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
128	19180.20	—	18962.82	18944.71	19710.36	19692.11
129	78.65	—	61.16	43.02	08.76	90.32
130	77.17		59.54	41.27	07.17	88.52
131	75.53		57.96	39.54	05.54	86.72
132	—		56.38	37.78	03.84	84.97
133			54.76	36.02	02.16	83.11
134			53.11	34.23	00.53	81.25
135			51.42	32.40	19698.86	79.36
136			49.73	30.61	97.15	77.28
137			48.08	28.82	95.48	75.21
138			46.36	26.95	93.78	—
139			44.71	25.20	92.11	
140			43.02	23.26	90.32	
141			41.27	—	88.52	
142			39.54		86.72	

procedure given in the previous chapter. The combination differences for the same vibrational level in different bands, are in good agreement within the experimental error and are given in Tables V and VI. Table VII gives the D_v values for the bands studied. The α_e values have been determined and it has been found that the value of α_e' is large as compared to α_e'' value. This is also supported by the calculated magnitudes obtained from the relation (Herzberg[11]):

$$\alpha_o = \frac{6\,(\omega_e x_e\ B_e^3)^{\frac{1}{2}}}{\omega_e} - \frac{6\,B_e^2}{\omega_e}$$

Table VIII gives the values of B_e, r_e and α_e of the two states involved.

An attempt was made to obtain the D_v values from the $\Delta_2F/(J+\frac{1}{2})$ versus $(J+\frac{1}{2})^2$ curves and to determine the B_v values more accurately therefrom. Because of the limit of our accuracy, the points are quite random and a straight line could not be drawn. However, taking an average of the three sets of $\Delta_2F''(J)$ values for the vibrational level $v'' = 0$, from (7, 0), (8, 0) and (9, 0) bands, the randomness of the points was reduced. The value of D_o'' was found out to lie in between 8×10^{-8} cm^{-1}

TABLE V

The combination differences for the (7, 0), (8, 0), (9, 0) and (10, 1) bands of the ^{79}Br molecule in wavenumbers.

J	7 - 0		8 - 0		9 - 0		10 - 1	
	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
54	7.25	9.06						
55	7.41	9.27						
56	7.57	9.47						
57	7.74	9.70						
58	7.93	9.92					7.83	9.80
59	8.12	10.12					7.91	10.12
60	8.29	10.35					8.15	10.44
61	8.47	10.50					8.41	10.72
62	8.55	10.71					8.64	10.99
63	8.71	10.89					8.69	11.21
64	8.87	11.09					8.82	11.35
65	9.03	11.26					8.96	11.49
66	9.15	11.46	9.09	11.67	9.08	-	9.05	11.67
67	9.28	11.60	9.19	11.85	9.25	11.81	9.18	11.80
68	9.41	11.79	9.37	12.03	9.39	12.07	9.27	12.03
69	9.56	11.96	9.46	12.22	9.50	12.30	9.46	12.07
70	9.75	12.19	9.65	12.35	9.60	12.32	9.55	12.26
71	9.95	12.47	9.73	12.58	9.70	12.47	9.69	12.49
72	10.13	12.64	9.87	12.67	9.85	12.66	9.83	12.72
73	10.26	12.80	10.01	12.86	9.99	12.82	10.08	12.81
74	10.39	12.98	10.19	12.99	10.09	13.00	10.10	13.03
75	10.55	13.12	10.23	13.26	10.27	13.17	10.28	13.18
76	10.67	13.30	10.42	13.40	10.37	13.30	10.33	13.40

TABLE V (Continued)

J	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
77	10.79	13.49	10.55	13.54	10.47	13.43	10.60	13.49
78	10.94	13.68	10.65	13.76	10.61	13.57	10.69	13.77
79	11.05	13.85	10.83	13.90	10.70	13.85	10.83	13.90
80	11.13	13.93	10.96	14.04	10.89	13.99	10.87	14.13
81	11.24	14.05	11.08	14.21	11.02	14.17	11.15	14.17
82	11.30	14.26	11.23	14.39	11.16	14.44	11.19	14.45
83	11.54	14.44	11.32	14.62	11.34	14.51	11.37	14.58
84	11.71	14.62	11.45	14.71	11.40	14.61	11.46	14.76
85	11.87	14.84	11.59	14.89	11.55	14.75	11.60	14.94
86	12.02	15.02	11.68	15.12	11.66	15.02	11.77	15.12
87	12.13	15.20	11.87	15.21	11.78	15.11	11.91	15.30
88	12.29	15.35	12.00	15.44	11.90	15.34	12.00	15.48
89	12.47	15.54	12.19	15.57	12.06	15.58	12.18	15.67
90	12.62	15.76	12.23	15.76	12.16	15.67	12.27	15.80
91	12.74	15.93	12.37	15.89	12.32	15.72	12.41	15.97
92	12.87	16.07	12.50	16.07	12.45	15.95	12.58	16.16
93	12.99	16.25	12.63	16.29	12.60	16.22	12.68	16.33
94	13.12	16.41	12.76	16.43	12.75	-	12.81	16.48
95	13.26	16.57	12.90	16.56	-		12.95	16.70
96	13.39	16.74	-	-			13.13	16.83
97	13.52	16.91					13.26	17.02
98	13.66	17.09					13.40	17.24
99	13.80	17.28					13.54	17.42
100	13.97	17.45					13.67	17.60

TABLE VI

The combination differences for the (7, 0), (8, 0), (9, 0) and (10, 1) bands of the $Bi^{81}Br$ molecule in wavenumbers.

J	7 - 0		8 - 0		9 - 0		10 - 1	
	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
63			8.44		8.57	11.08	8.56	11.01
64			8.52	11.01	8.67	11.21	8.60	11.08
65	9.01		8.67	11.18	8.80	11.31	8.71	11.21
66	9.18	11.38	8.80	11.34	8.85	11.40	8.86	11.37
67	9.28	11.60	8.94	11.51	9.00	11.54	8.95	11.57
68	9.32	11.73	9.08	11.69	9.18	11.69	9.09	11.66
69	9.42	11.80	9.17	11.84	9.23	11.81	9.23	11.84
70	9.50	11.97	9.37	12.01	9.28	12.01	9.31	12.09
71	9.82	12.26	9.59	12.25	9.41	12.15	9.50	12.20
72	9.92	12.43	9.68	12.44	9.51	12.19	9.68	12.39
73	9.90	12.55	9.78	12.62	9.55	12.38	9.78	12.57
74	10.08	12.59	9.95	12.76	9.78	12.65	9.91	12.76
75	10.22	12.80	10.05	12.93	9.96	12.83	10.05	12.94
76	10.38	13.03	10.18	13.03	10.14	12.92	10.23	13.07
77	10.58	13.11	10.27	13.25	10.27	13.15	10.32	13.35
78	10.63	13.29	10.41	13.47	10.37	13.42	10.50	13.44
79	10.74	13.59	10.59	13.57	10.55	13.56	10.55	13.57
80	10.96	13.68	10.72	13.76	10.78	13.70	10.68	13.75
81	11.07	13.87	10.82	13.93	10.83	13.98	10.86	13.93
82	11.24	14.01	10.95	14.07	10.88	14.11	10.95	14.12
83	11.40	14.21	11.09	14.23	11.06	14.16	11.09	14.20
84	11.49	14.40	11.25	14.38	11.20	14.39	11.18	14.34

TABLE VI (Continued)

J	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''	Δ_2F'	Δ_2F''
85	11.59	14.54	11.31	14.61	11.38	14.62	11.22	14.61
86	11.81	14.60	11.41	14.75	11.47	14.80	11.49	14.70
87	11.98	14.94	11.59	14.84	11.61	14.89	11.63	14.93
88	12.06	15.13	11.67	15.06	11.74	15.12	11.73	15.10
89	12.19	15.25	11.85	15.19	11.92	15.30	11.85	15.20
90	12.34	15.38	11.94	15.37	12.02	15.48	11.94	15.42
91	12.44	15.59	12.09	15.56	12.20	15.76	12.17	15.56
92	12.62	15.76	12.26	15.66	12.43	15.99	12.31	15.78
93	12.76	15.95	12.30	15.92	12.57	16.08	12.35	16.01
94	12.90	16.09	12.48	16.01	12.66	16.22	12.53	16.06
95	12.99	16.26	12.67	16.23	12.80	16.36	12.62	16.28
96	13.11	16.42	12.76	16.46	12.85	-	12.81	16.41
97	13.27	16.63	12.94	16.60	-		12.94	16.60
98	13.44	16.75	13.04	16.77			13.03	16.82
99	13.56	16.96	13.16	16.96			13.20	17.00
100	13.81	17.13	13.39	-			13.39	-

TABLE VII

The B'_v and B''_v values of the different bands studied.

v' v''	$Bi^{79}Br$		$Bi^{81}Br$	
	B'_v cm^{-1}	B''_v cm^{-1}	B'_v cm^{-1}	B''_v cm^{-1}
0 , 7	0.0363	0.0425	0.0357	0.0416
0 , 6	0.0363	0.0426_5	0.0357	0.0419_5
7 , 0	0.0345	0.0436	0.0338_5	0.0428
8 , 0	0.0342_5	0.0436	0.0336	0.0428
9 , 0	0.0340	0.0436	0.0334	0.0428
10 , 1	0.0338	0.0433_5	0.0331_5	0.0426_5
1 , 4	0.0361	0.0429_5	0.0355_5	0.0422

TABLE VIII

The molecular constants obtained for BiBr.

	$Bi^{79}Br$	$Bi^{81}Br$
B_o'	0.0364_2 cm^{-1}	0.0358_2 cm^{-1}
B_o''	0.0430_7 cm^{-1}	0.0428_7 cm^{-1}
r_o'	2.64_2 Å	2.64 Å
r_o''	2.59_6 Å	2.59_6 Å

	Observed	Calculated
$\alpha_e' =$	0.00025 cm^{-1}	0.00017 cm^{-1}
$\alpha_e'' =$	0.00015 cm^{-1}	0.00012 cm^{-1}

$D_o'' = 5.0 \pm 4.0 \times 10^{-8} cm^{-1}$; $D_e'' = 0.76 \times 10^{-8}$ cm^{-1}

and 1×10^{-6} cm^{-1}.

The calculated value of D_o^o from the relation (Herzberg[11]) is 0.8×10^{-6} cm^{-1}.

THE ELECTRONIC TRANSITION INVOLVED:

The lowest electronic configurations for the two atoms are :

$$Bi - (KLMNO5pd)\ 6s^2\ 6p^3 - (^4S_{3/2})$$
$$Br - (KLM)\ 4s^2\ 4p^5 - (^2P_{3/2})$$

Following Mulliken's[12] notation the ground state electronic configuration for the BiBr molecule may be written as:

$$(KKLLMM\ NO5pd)(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)^2,$$

which gives rise to the following electronic terms:

$$^3\Sigma^- (0^+, 1),\ ^1\Delta(2) \text{ and } ^1\Sigma^+(0^+).$$

Out of these three $^3\Sigma^-$ $(0^+, 1)$ is expected to lie lowest according to Hund's rule. The ground state of the molecule is very likely the lower state of the present band system (4600 Å - 6063 Å) as Morgan[2] has also observed this system in absorption.

The first excited state has been derived for the analogous visible band system of the BiCl molecule by Khanna[9] to be

$$(KK\sigma_{3d})(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)(u\sigma)\,{}^3\pi(0^+),$$

where $v\pi$ was represented as an antibonding orbital of the type $(6p\pi_{Bi} - 4p\pi_{Br})$ and $(u\sigma)$ an antibonding orbital of the type $(6p\sigma_{Bi} - 4p\sigma_{Br})$. In case of the PbBr molecule, which has one electron less than BiBr, it has been said in the previous chapter that the character of the $(v\pi)$ orbital should be nonbonding (Barrow and others[13]). It is more likely that the $(v\pi)$ orbital may be bobbonding and $(u\sigma)$ an antibonding for the BiBr molecule as well. The decrease in vibrational frequency in the excited state A as compared to the ground state X of the BiBr molecule, substantiates the above argument.

Taking into consideration the fact that the structure of the bands contains only P and R branches it is very likely that the transition involved is $^3\pi(0^+) - {}^3\Sigma^-(0^+)$, given by the configuration:

$$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)(u\sigma) - {}^3\pi(0^+)$$

$$\longrightarrow (z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)^2 - {}^3\Sigma^-(0^+),$$

where the coupling is of Hund's case (c) type.

REFERENCES

1.	Howell, H.G. and Rochester, G.D.	Univ.Durham Phil.Soc. Proc. 9, 126 (1934).
2.	Morgan, F.	Phys.Rev., 49, 41 (1936).
3.	Sur, P.K. and Majumdar, K.	Proc.Natl.Inst.Sci.Ind. 20, 235 (1954).
4.	Sankaranarayanan, S., Patel, M.M. and Narayanan, P.S.	Proc.Ind.Acad.Sci. 56, 171 (1962).
5.	Khanna, D.N.	J.Mol.Spectroscopy, 6, 319 (1961).
6.	Murty, P.S. and Rao, P.T.	Curr.Sci., 37, 161 (March, 1968).
7.	Harrison, G.R.	M.I.T.Table (New York: John Wiley), 1939.
8.	"Table of Wavenumbers"	N.B.S.Monograph No.3, Vol.1, National Bureau of Standards, Washington, D.C, (1960).
9.	Rao, V.S. and Rao, P.T.	Z.Physik, 181, 50 (1964).
10.	Lal, K.M. and Khanna, D.N.	Can.J.Phys., 45, 3663 (1967)
11.	Herzberg, G.	Spectra of Diatomic Molecules, 2nd Edn.(New York: D.Van Nostrand), (1950).
12.	Mulliken, R.S.	Rev.Mod.Phys. 4, 1 (1932).
13.	Barrow, R.F., Butler, D., Johns, J.W.C, and Powell, J.L.	Proc.Phys.Soc.(Lond.) 73, 317 (1959).

CHAPTER III

Rotational Analysis of the D-X System of the InCl Molecule.

ABSTRACT

The emission spectrum of the InCl molecule has been excited and the bands lying in the near ultraviolet region (3400 Å – 3650 Å) have been photographed in the second order of a 35 ft concave grating spectrograph. The rotational lines of the (0, 0), (0, 1) and (1, 0) bands of the B–X system have been identified and their wavenumbers determined. The analyses of the bands have been carried out leading to the determination of the following constants for $In^{115}Cl^{35}$ molecule:

$B_e' = 0.1150\ cm^{-1}$; $B_e'' = 0.1093\ cm^{-1}$

$r_e' = 2.330$ Å ; $r_e'' = 2.399$ Å

$\alpha_e' = 8 \times 10^{-4}\ cm^{-1}$ $\alpha_e'' = 5 \times 10^{-4}\ cm^{-1}$

$D_e' = 3.0 \times 10^{-8}\ cm^{-1}$; $D_e'' = 2.4 \times 10^{-8}\ cm^{-1}$.

The value of the ground state internuclear distance agrees with that obtained by Youngner and Winans from the absorption experiment. The probable electronic configurations for the states involved in the transition of this band system have been arrived at from a correlation of the united and separated atom model approach.

INTRODUCTION

The molecular spectrum of Indium monochloride was first recorded by Grotrian[1] who obtained a band system appearing in the region 2650 Å - 2800 Å while studying the absorption of Indium vapour. He interpreted these bands as being due to a weakly bound In_2 molecule. The same spectrum was obtained again by Waring[2] in the absorption through indium and cadmium vapours. He suggested that the spectrum was probably due to InCd molecule. Winans, Davis and Leitzke[3] observed this band system again in absorption through a mixture of mercury and indium vapours. Using bismuth vapour ., Barrat and Bonar[4] observed several bands in absorption whose wavelengths agreed with those reported by Waring[2] and they, therefore, attributed them to Bi_2 molecule. Wehrli and Miescher[5] were the first to obtain these bands under sufficient dispersion and to positively identify them as due to the Indium monochloride molecule. They recorded three band systems; The system A (3470 Å - 3640 Å), the system B (3370 Å - 3540 Å) and the system C in 2650 Å region. Froslie and Winans[6] made a detailed rotational analysis of the bands lying in 2650 Å - 3000 Å region, referred by them as the fundamental system. The spectrum was recorded in absorption in

the fourth order of a 21 ft grating spectrograph, which gave a disperaion of approximately 0.6 Å/mm. They also photographed the intercombination system lying in the region 3300 Å - 3700 Å in the third order of the grating but could not perform the rotational analysis because of overlapping in this region.

Youngner and Winans[7] photographed the absorption spectra of InCl using 8 metre absorption cell, containing the vapour of Indium Chloride, in the third order of a 21 ft concave grating spectrograph. The reciprocal dispersion was 0.773 Å/mm and the resolving power obtained was 2,20,000. The rotational lines of the (0, 0), (0, 1) and (1, 0) bands of the A-X system and the (0, 0) band of the B-X system were identified and measured. They performed the rotational analysis of the bands and gave the rotational constants for the states A and X. In contrast to the value of the internuclear distance (r_o = 2.321 Å) for the ground state obtained by Frosliod and Winans[6], the value obtained by Youngner and Winans[7] (r''_o = 2.399 Å) agrees, within the range of experimental error, with the value r''_o = 2.4011 Å obtained from the microwave absorption experiment by Barrett and Mandel[8]. Youngner and Winans[7] utilised the structure of the (0, 0)

band of the B-X system for the rotational analysis of the A-X system as it was easy to determine the numbering of the Q branch in the (0, 0) band of the B-X system and find out rotational constants for the ground state. The B values for the (0, 0) band of the B-X system are given by them.

In order to complete the rotational analysis of the B-X system the present investigation was undertaken. The structure of all the bands of InCl lying in the region 3400 Å - 3650 Å was recorded in emission in the second order of a 35 ft grating spectrograph having a theoretical resolution of 3,60,000 and the rotational lines of the (0, 0), (1, 0) and (0, 1) bands of the B-X system were identified and measured. The structure of the other bands is quite overlapped for any accurate measurements. All the bands of this system show the presence of a strong Q branch — one P and one R branch. The rotational analysis of these bands is given in this chapter alongwith the corresponding discussion. The electronic transition involved in the system is also discussed.

EXPERIMENTAL DETAILS

The emission spectrum of InCl was first excited in a discharge tube, having cylindrical nickel electrodes placed coaxially along the length of the discharge tube, 20 cm in length and 8 mm in diameter. Pure sample of Indium metal in pieces was placed along the length of the tube and dehydrated sample of cupric chloride was placed near the electrodes to extract necessary chlorine. First the discharge tube was evacuated and filled with helium gas approximately at 30 mm pressure. The metal was vaporised by an uncondensed transformer discharge applying 4000 volts, with an eight kilowatt power transformer. The discharge tube near the electrodes got heated sufficiently to evolve necessary chlorine. The colour of the discharge was intense violet. The intensity of the source was so strong that it required only a minute to record the near ultraviolet systems on a medium quartz spectrograph. The band system lying in the region 2650 Å - 2000 Å, appeared quite weak in emission. As the discharge was a closed one the life of the tube was very short and one tube lasted for 30 minutes only. Later another technique was developed to excite the band system where the discharge tube ran for hours.

Pure sample of $InCl_3$ was kept in an U tube made of quartz and 3 mm in diameter as described in previous chapters and excited with the help of a 2450 Mc/sec microwave generator. The heat generated by the microwave discharge was sufficient to melt and excite the vapours. Spectra obtained from both the techniques were the same except for the only difference that the intensity of the source excited by microwave generator was weaker as compared to the transformer discharge. The exposure time to record the spectrum in the second order of a 35 ft concave grating spectrograph ranged from 45 minutes to one hour for the transformer discharge and 4 to 8 hours for microwave discharge. The spectra were easily recorded as the grating was blazed at 7500 Å in the first order. All the bands lying in the region 3400 Å - 3650 Å were recorded on Ilford Q-2 and ORWO Ultraviolet plates. Iron arc spectrum was used as the comparison spectrum. The dispersion obtained in this region was 0.35 Å/mm. The accuracy of measurement as mentioned previously is of the order of $\pm$ 0.04 cm^{-1} for sharp lines and $\pm$ 0.10 cm^{-1} for broad diffuse lines in this case too.

EXPERIMENTAL DATA AND ROTATIONAL ANALYSIS

All the bands of this system are violet degraded

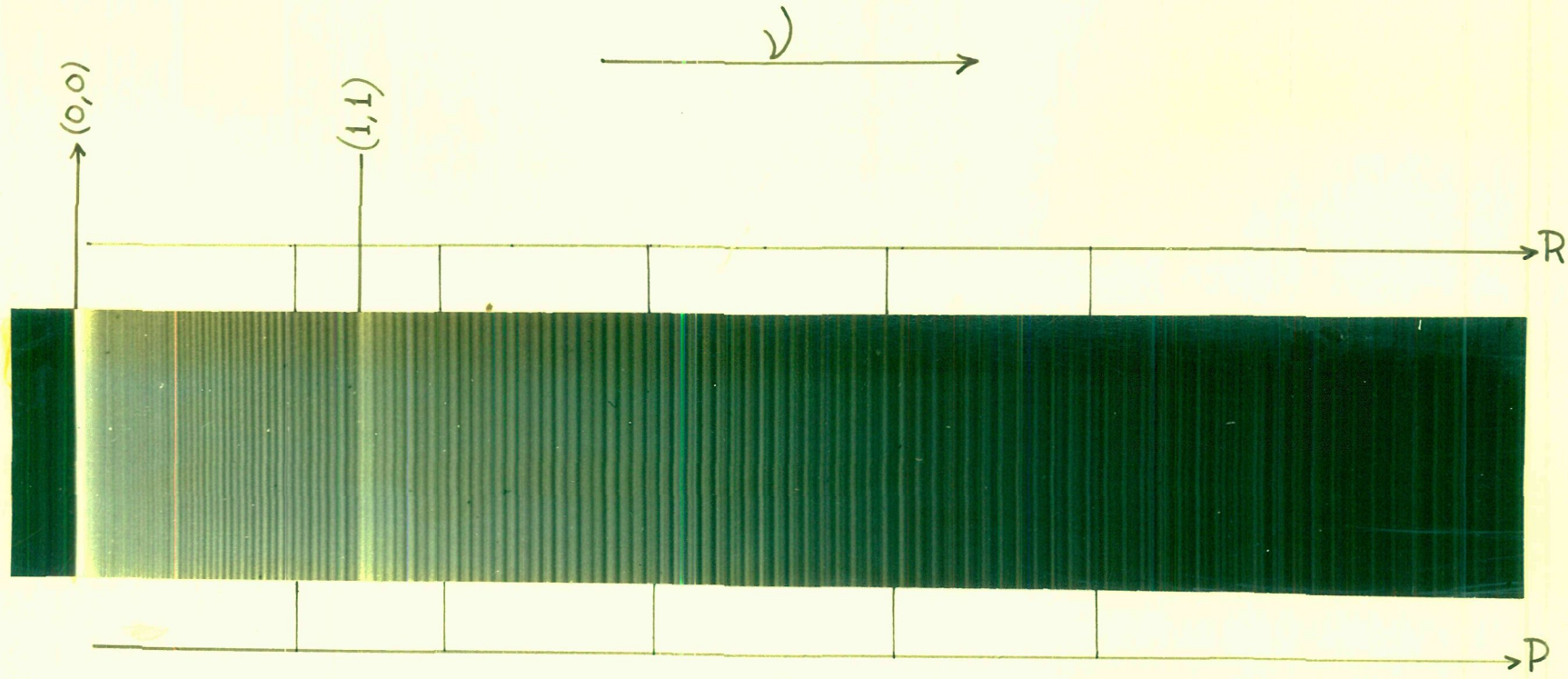

Fig. 1. The Enlargement of the (O, O) band of the A-X System (3470-3640Å) of InCl (35 ft grating II order).

the head on the shorter wavelength side being the strong Q head. In the $\Delta v = 0$ sequence the first member is very intense as compared to the (1, 1) band and the other members are absent. The $\Delta v = +1$ and $\Delta v = -1$ sequences have got four to five members each, all of them are quite strong but so close to each other that it is possible to measure the rotational structure of the first member only. The $\Delta v = +2$ sequence is too weak to be recorded at the high resolution. Thus three bands (0, 0), (1, 0) and (0, 1) have been chosen for the rotational analysis. The enlarged reproduction of the (0, 0) bands of the A-X and B-X systems are given in Figs.1 and 2 respectively. The structure of the A (0, 0) band shows the presence of only two branches as observed by Youngner and Winans[7]. It is seen very clearly from Fig.2 that the structure of the B (0, 0) band consists of single P, Q and R branches. Near the band head there is a single series of lines which slowly gets broadened and a weak branch P is resolved. At a considerable distance from the band head a relatively intense R branch separates out from the Q branch and at this point the returning P branch fades out.

The B (0, 0) Band

The Q branch of this band was first sorted out

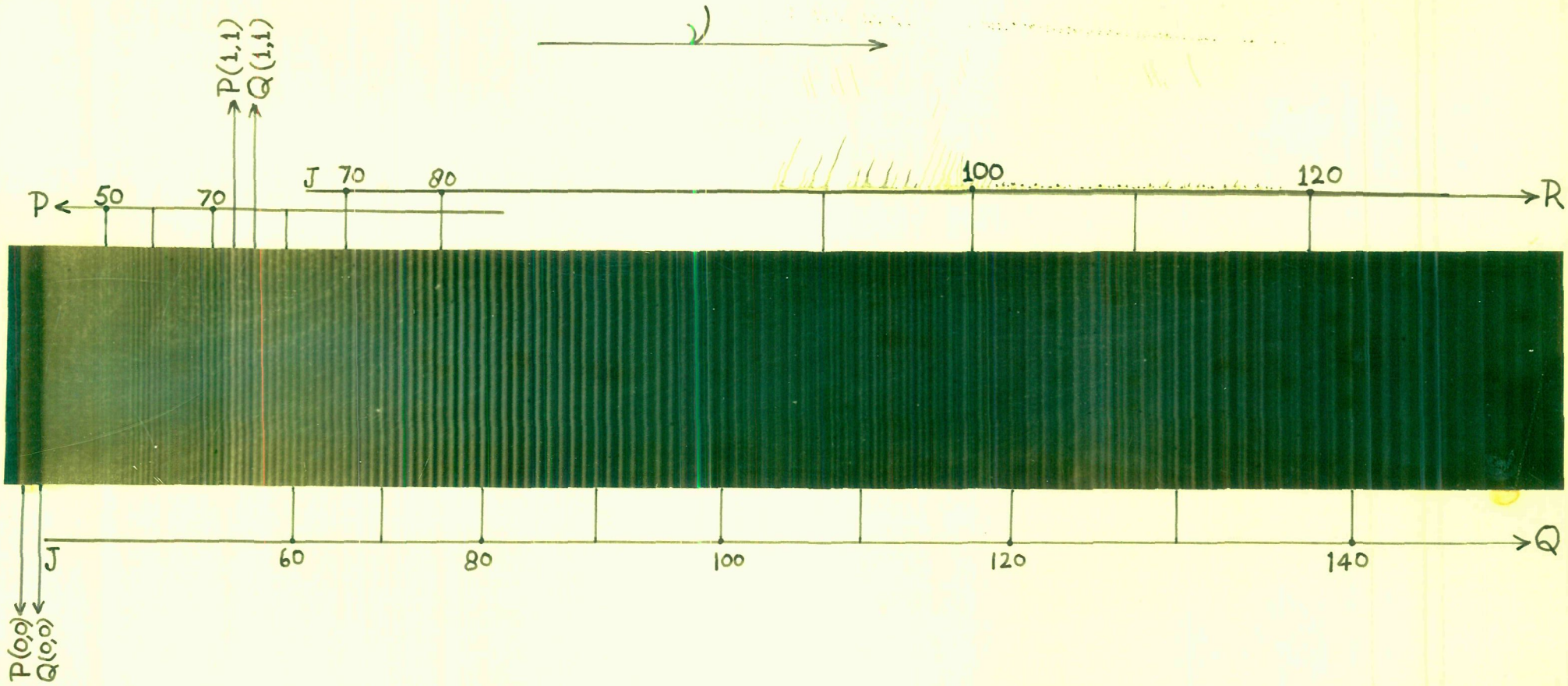

Fig. 2. The Enlargement of the (0, 0) band of the B-X System(3370-3540 Å) of InCl (35 ft grating II order).

and a systematic discrepancy (~ 0.1 cm^{-1}) was found in the position of the lines observed presently and those reported by Youngner and Winans[7]. The relative numbering of the branches has been obtained by systematic trials until the relations

$$R(J) = Q(J) = Q(J+1) = P(J+1) = \Delta_1 F' \quad \ldots\ldots(1)$$

and $$R(J) = Q(J+1) = Q(J) = P(J+1) = \Delta_1 F'' \quad \ldots\ldots(2)$$

were fulfilled for all J values. The absolute J numbering has been fixed from the $\Delta_1 F(J)$ versus J graph such that the straight line cuts the abscissa axis at $J = -1$. The present J numbering differs by unity from the numbering given by Youngner and Winans[7]. The absolute numbering of the Q branch was verified by the following procedure:

The Q branch is represented by the formula (Herzberg[9], page 136)

$$Q(J) = \nu_0 + (B'_v - B''_v)J(J+1) \quad \ldots\ldots(3)$$

for low J values. If Q(J) is plotted against J(J+1), a straight line is obtained whose intersection with the ordinate axis gives the band origin and whose slope gives $(B'_v - B''_v)$. Taking the values of Q(J), as given by Winans[7]

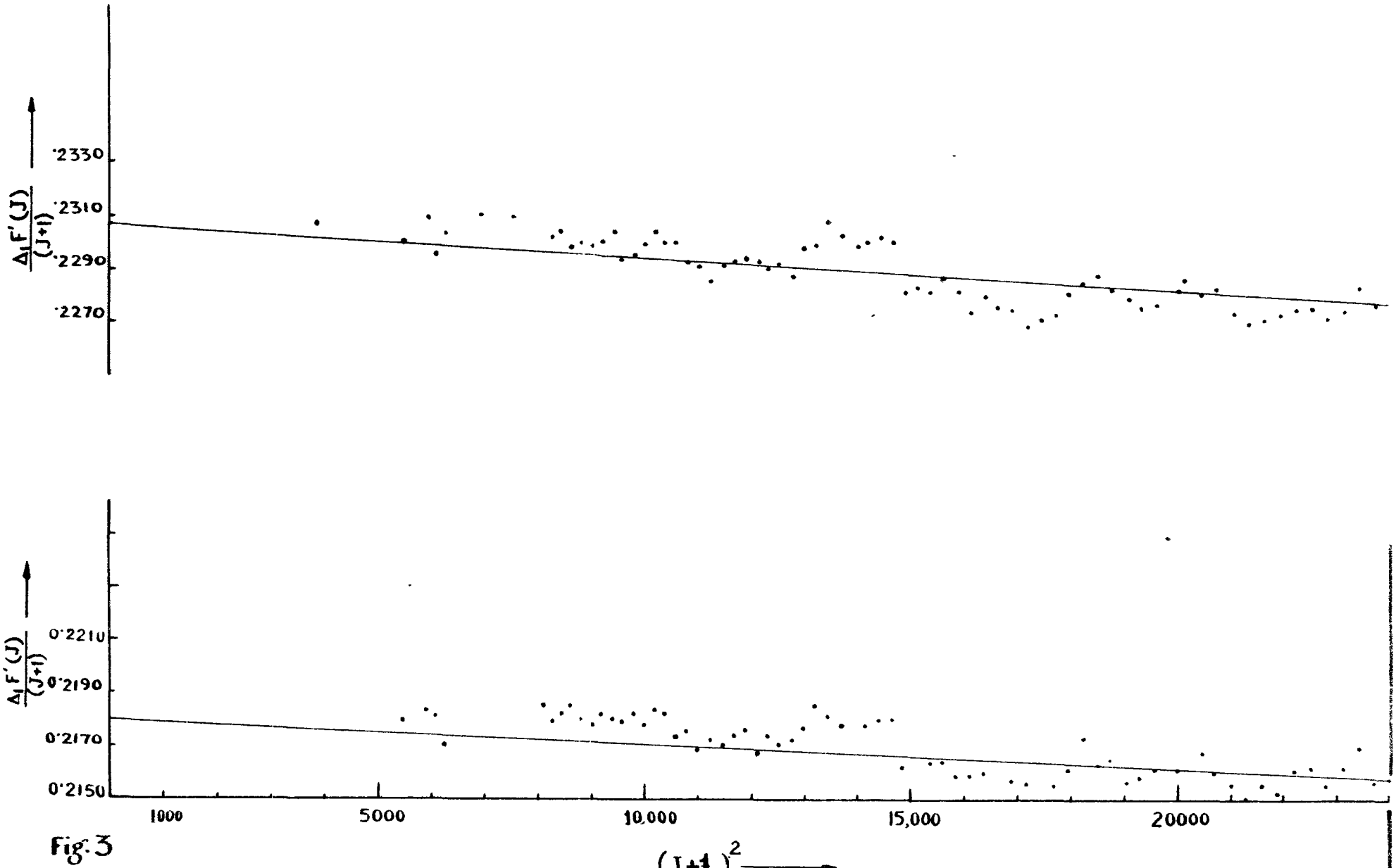

Fig. 3

GRAPHICAL DETERMINATION OF B_v AND D_v FOR THE (0,0) BAND OF THE B–X SYSTEM.

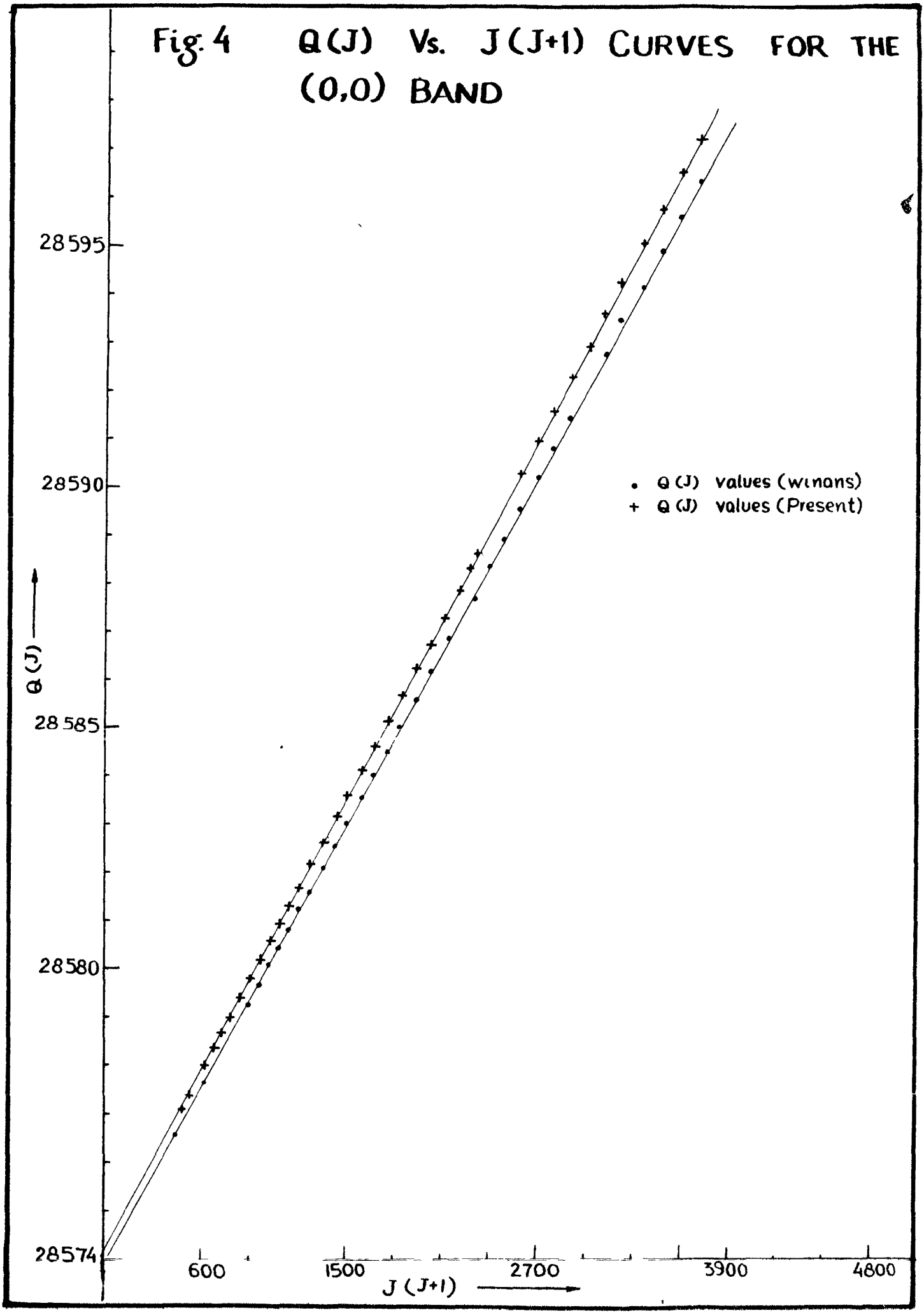
Fig. 4 Q(J) Vs. J(J+1) CURVES FOR THE (0,0) BAND
28595
28590
28585
28580
28574
Q(J)
600
1500
2700
3900
4800
J(J+1)
• Q(J) values (Winans)
+ Q(J) values (Present)

the curve has been plotted and the value of the band origin comes out to lie at 28573.9 cm^{-1} (Fig.4). The measured value of Youngner and Winans[7] for the Q head of this band is 28574.27 cm^{-1}. Thus, there is a difference of 0.37 cm^{-1} between the observed value of the band origin and that obtained from the abovementioned graph, which differs by an amount much greater than the experimental error involved in their measurements. The band origin obtained using the present assignment and Q(J) values is 28574.1 cm^{-1} which is in a good agreement with the observed Q head lying at 28574.11 cm^{-1} from the present measurements.

The wavenumbers of the lines, assignments and combination differences are given in Table I. The two values of $\Delta_1 F'$ and $\Delta_1 F''$ obtained from the relations (1) and (2) agree within the range of experimental error, except for the places where the lines are broad due to the overlapping of the branches.

The constants were determined from the intercepts and slopes of the graph (Fig.3.)

$\Delta_1 F'(J)/(J+1)$ versus $(J+1)^2$

and $\Delta_1 F''(J)/(J+1)$ versus $(J+1)^2$

TABLE I. Vacuum Wavenumbers, Rotational Assignments and Combination Differences for the (0, 0) band of $In^{115}Cl^{35}$ molecule.

J	R(J)	Q(J)	P(J)	$\frac{R(J)-Q(J)}{\Delta_1F''}$	$\frac{Q(J+1)-P(J+1)}{\Delta_1F'}$	$\frac{R(J)-Q(J+1)}{\Delta_1F'}$	$\frac{Q(J)-P(J+1)}{\Delta_1F''}$
17		28576.07					
18		76.32					
19		76.56					
20		76.89					
21		77.13					
22		77.46					
23		77.79					
24		78.03					
25		78.36					
26		78.68					
27		79.09					
28		79.42					
29	28587.27	79.83		7.44		7.03	
30	87.84	80.24	-	7.60	-	7.19	-
31	88.41	80.65	-	7.76	-	7.44	-

TABLE I (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F'	Δ_1F'	Δ_1F''	Δ_1F''
32	20589.06	20580.97		8.09	8.01	7.76	7.68
33	89.72	81.30	20573.29	8.42	8.33	7.93	7.84
34	90.29	81.79	73.46	8.50	8.50	8.09	8.09
35	90.94	82.20	73.70	8.74	8.68	8.25	8.33
36	91.60	82.69	73.87	8.91	-	8.42	-
37	92.25	83.18	-	9.07	-	8.58	-
38	92.91	83.67	-	9.24	-	8.75	-
39	93.64	84.16	-	9.48	-	8.99	-
40	94.30	84.65	-	9.65	9.56	9.16	9.07
41	95.03	85.14	20573.58	9.89	9.80	9.32	9.23
42	95.77	85.71	75.91	10.06	9.96	9.69	9.39
43	96.51	86.28	76.32	10.23	10.13	9.82	9.72
44	97.24	86.69	76.56	10.55	10.38	9.97	9.80
45	98.06	87.27	76.89	10.79	10.71	10.22	10.14
46	98.88	87.84	77.13	11.04	10.95	10.47	10.38
47	99.70	88.41	77.46	11.29	11.27	10.64	10.62
48	20600.51	89.06	77.79	11.48	11.36	10.79	10.70
49	01.41	89.72	78.36	11.69	11.41	11.12	11.04

TABLE I (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F^1	Δ_1F^1	Δ_1F^e	Δ_1F^e
50	28602.15	23590.29	28578.68	11.86	11.85	11.21	11.20
51	03.05	90.94	79.09	12.11	12.18	11.45	11.52
52	03.95	91.60	79.42	12.35	12.42	11.70	11.77
53	04.85	92.25	79.83	12.60	12.67	11.94	12.01
54	05.83	92.91	80.24	12.92	12.99	12.19	12.26
55	06.65	93.64	80.65	13.01	13.00	12.35	12.34
56	07.50	94.30	81.30	13.25	13.24	12.52	12.51
57	08.53	95.03	81.79	13.50	13.57	12.76	12.83
58	09.44	95.77	82.20	13.67	13.82	12.93	13.08
59	10.42	96.51	82.69	13.92	14.06	13.18	13.33
60	11.40	97.24	83.18	14.16	-	13.34	-
61	12.38	98.06	-	14.32	-	13.60	-
62	13.38	98.78	-	14.60	14.00	13.93	14.13
63	14.40	99.45	28584.65	14.95	15.13	14.13	14.31
64	15.58	28600.27	85.14	15.31	15.38	14.49	14.56
65	16.56	01.09	85.71	15.47	-	14.66	-
66	17.54	01.90	-	15.64	15.45	14.82	14.63
67	18.61	02.72	28587.27	15.89	15.70	15.07	14.88

TABLE I (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F^e	Δ_1F^f	Δ_1F^e	Δ_1F^f
68	28619.67	28603.54	28587.84	16.13	16.03	15.23	15.13
69	20.66	04.44	88.41	16.22	16.28	15.32	15.38
70	21.80	05.34	89.06	16.46	16.44	15.64	15.62
71	22.87	06.16	89.72	16.71	16.77	15.81	15.87
72	23.93	07.06	90.29	16.87	17.10	15.89	16.12
73	25.08	08.04	90.94	17.04	-	16.14	-
74	26.23	08.94	-	17.29	17.42	16.39	16.52
75	27.38	09.84	28592.42	17.54	17.68	16.63	16.77
76	28.44	10.75	93.07	17.69	17.92	16.71	16.94
77	29.59	11.73	93.81	17.86	17.99	16.96	17.09
78	30.74	12.63	94.64	18.11	18.31	17.05	17.25
79	32.13	13.69	95.38	18.44	18.58	17.54	17.68
80	33.36	14.59	96.01	18.77	18.83	17.76	17.84
81	34.67	15.58	96.75	19.09	18.99	18.11	18.01
82	35.82	16.56	97.57	19.26	19.15	18.28	18.17
83	37.05	17.54	98.39	19.51	19.49	18.44	18.42
84	38.36	18.61	99.12	19.75	-	18.69	-
85	39.60	19.67	-	19.93	20.15	18.94	19.16

TABLE I (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F^e	Δ_1F^f	Δ_1F^e	Δ_1F^f
86	28640.91	28620.66	28600.51	20.25	20.39	19.11	19.25
87	42.14	21.80	01.41	20.34	-	19.27	-
88	43.53	22.87	-	20.66	-	19.60	-
89	44.77	23.93	-	20.84	-	19.69	-
90	46.14	25.08	-	21.06	20.89	19.91	19.75
91	47.47	26.23	28605.34	21.24	21.22	20.09	20.07
92	48.79	27.38	06.16	21.41	21.38	20.35	20.32
93	50.18	28.44	07.06	21.74	21.55	20.59	20.40
94	51.50	29.59	08.04	21.91	21.80	20.76	20.65
95	52.89	30.74	08.94	22.15	22.05	21.00	20.90
96	54.29	31.89	09.84	22.40	22.37	21.17	21.14
97	55.68	33.12	10.75	22.56	22.62	21.33	21.39
98	57.00	34.35	11.73	22.65	22.86	21.51	21.72
99	58.48	35.49	12.63	22.99	23.03	21.76	21.80
100	59.96	36.72	13.69	23.24	23.36	22.01	22.13
101	61.44	37.95	14.59	23.49	23.50	22.26	22.27
102	62.91	39.18	15.68	23.73	23.71	22.41	22.39
103	64.39	40.50	16.79	23.89	23.86	22.66	22.63

TABLE I (Continued)

J	R(J)	Q(J)	P(J)	$\Delta_1 F'$	$\Delta_1 F'$	$\Delta_1 F^*$	$\Delta_1 F^*$
104	28665.87	28641.73	28617.87	24.14	24.02	22.83	22.71
105	67.35	43.04	19.02*	24.31	24.19	23.08	22.96
106	68.91	44.27	20.08*	24.64	24.44	23.32	23.12
107	70.48	45.59	21.15*	24.89	24.69	23.58	23.38
108	72.04	46.90	22.21*	25.14	24.93	23.83	23.62
109	73.60	48.21	23.28*	25.39	25.10	23.99	23.70
110	75.16	49.61	24.51*	25.55	25.35	24.24	24.04
111	76.73	50.92	25.57*	25.81	25.60	24.41	24.20
112	78.29	52.32	26.72*	25.97	25.76	24.66	24.45
113	79.85	53.63	27.87*	26.22	-	24.82	-
114	81.50	55.03	-	26.47	-	25.16	-
115	83.14	56.34	-	26.80	-	25.32	-
116	84.79	57.82	-	26.97	-	25.49	-
117	86.35	59.30	-	27.05	27.25	25.74	25.94
118	88.00	60.61	33.36	27.39	27.42	25.99	25.94
119	89.65	62.09	34.67	27.56	27.75	26.08	26.27
120	91.29	63.57	35.82*	27.72	28.00	26.24	26.52
121	93.02	65.05	37.05*	27.97	27.76	26.49	26.28

TABLE I (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F'	Δ_1F'	Δ_1F''	Δ_1F''
122	28694.67	28666.53	28638.77	28.14	28.08	26.58	26.38
123	96.48	68.09	40.01	28.39	28.25	26.91	26.77
124	98.29	69.57	41.32	28.72	28.50	27.16	26.94
125	99.94	71.13	42.63	28.81	28.76	27.24	27.19
126	28701.59	72.70	43.94	28.89	28.92	27.41	27.44
127	03.40	74.18	45.26	29.22	-	27.66	-
128	05.13	75.74	-	29.39	-	27.74	-
129	06.95	77.39	-	29.56	29.67	28.00	28.11
130	08.68	78.95	28649.28	29.73	-	28.29	-
131	10.41	80.43	-	29.98	30.00	28.34	28.36
132	12.31	82.07	28652.07	30.24	-	28.67	-
133	14.24	83.64	-	30.60		28.96	
134	16.18	85.28		30.90		29.33	
135	18.00	86.89		31.15		29.42	
136	19.89	88.58		31.31		29.67	
137	21.71	90.22		31.49		29.76	
138	23.61	91.95		31.66		30.00	
139	25.51	93.60		31.91		30.26	

TABLE I(Continued)

J	R(J)	Q(J)	P(J)	Δ_1F'	Δ_1F'	Δ_1F''	Δ_1F''
140	28727.40	28695.25	—	32.15	—	30.51	—
141	29.39	96.89	—	32.50	—	30.77	—
142	31.28	98.62		32.66		31.01	
143	33.18	20700.27		32.91		31.10	
144	35.08	02.08		33.00		31.26	
145	36.98	03.82		33.16		31.35	
146	39.05	05.63		33.42		31.69	
147	41.03	07.36		33.67		31.86	
148	43.10	09.17		33.93		32.20	
149	45.08	10.90		34.18		32.44	
150	46.98	12.64		34.34		32.55	
151	49.05	14.43		34.62		32.87	
152	51.20	16.18		35.02		33.20	
153	53.10	18.00		35.10		33.21	
154	55.17	19.99		35.28		33.46	
155	57.24	21.71		35.53		33.63	
156	59.30	23.61		35.69		33.79	
157	61.37	25.51		35.86		33.97	
158	63.19	27.40		-		-	

* These lines are broad due to overlapping.

It has been found that the value of B_o'' is the same as reported by Youngner and Winans[7], but the value of B_o' is slightly different.

$$B_o' = 0.1154 \text{ cm}^{-1} \text{ (Present)}$$
$$= 0.1152 \text{ cm}^{-1} \text{ (Winans)}$$
$$B_o'' = 0.1090 \text{ cm}^{-1} \text{ (Present)}$$
$$= 0.1090 \text{ cm}^{-1} \text{ (Winans)}$$

The slope of the straight line from the graph of Q(J) versus J(J+1) (Fig. 4) gives the value

$$B_o' - B_o'' = 0.0064 \text{ cm}^{-1}$$

which is also the difference between the B values determined from $\Delta_1 F(J)/(J+1)$ versus $(J+1)^2$ graphs.

The (0, 1) and (1, 0) Bands

The assignment for the branches of (0, 1) and (1, 0) bands has been done in the way described for the (0, 0) band. It is possible to measure Q lines upto J = 70 only for both the bands due to the overlapping of equally intense (1, 2) and (2, 1) bands. The wave-numbers, assignments and combination differences for the

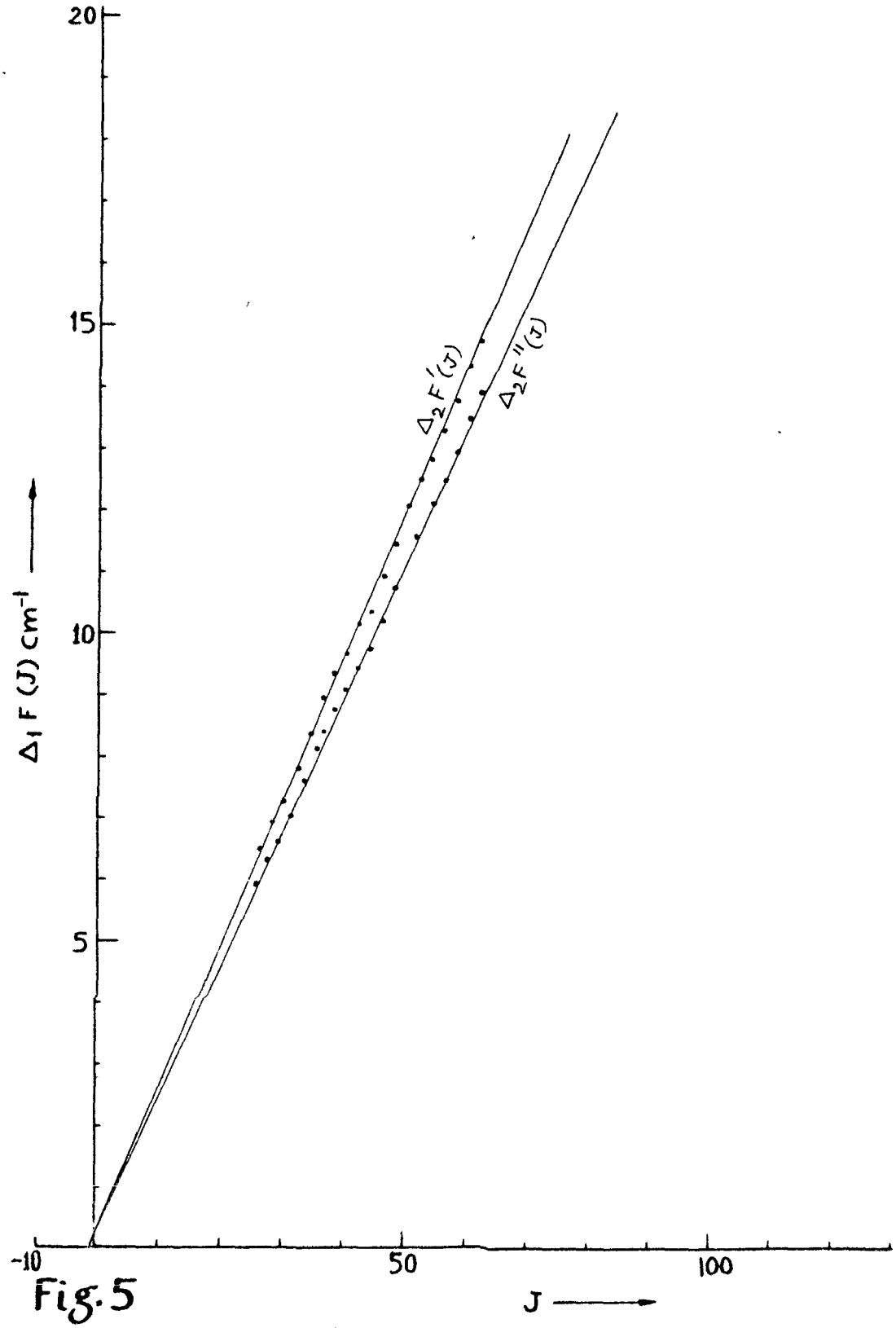

Fig. 5

$\Delta_1 F(J)$ Vs. J CURVES FOR THE (0,1) BAND

bands are given in Tables II and III. The number of the combination differences i.e. $\Delta_1 F$ values, is very small for these bands and the constants have been determined from the $\Delta_1 F(J)$ versus J curves (Fig. 5).

The B values of all the bands alongwith the values of α_e and D_v values are given in Table IV.

As the transition is a $\Pi - \Sigma$ one, the combination defect should be observed. However, for the (0, 0) band in most of the cases the values $R(J) - Q(J)$ is greater than the values of $Q(J+1) - P(J+1)$ as the case should be. Similarly

$$R(J) - Q(J+1) > Q(J) - P(J+1)$$

for most of the cases.

THE ELECTRONIC TRANSITION INVOLVED

It has already been said by the previous workers (Mieschor[10], Wehrli and Mieschor[5], Youngner and Winans[7]) that the near ultraviolet systems which appear in the case of Indium and Thallium halides belong to a $^3\Pi - {}^1\Sigma$ transition. The three components of $^3\Pi$ state are well separated from each other and at least two separate band

TABLE II. Vacuum Wavenumbers, Rotational Assignments and Combination Differences for the (0, 1) band of $In^{115}Cl^{35}$ Molecule.

J	R(J)	Q(J)	P(J)	$\frac{R(J)-Q(J)}{\Delta_1 F'}$	$\frac{Q(J+1)-P(J+1)}{\Delta_1 F''}$	$\frac{R(J)-Q(J+1)}{\Delta_1 F^{IV}}$	$\frac{Q(J)-P(J+1)}{\Delta_1 F^{III}}$
10	28263.01	28260.20		2.81		2.56	
11	63.41	60.45		2.96		2.70	
12	-	60.71		-		-	
13	-	60.97		-		-	
14	28264.96	61.23		3.73		3.48	
15	64.56	61.48		4.08		-	
16	-	61.75		-		-	
17	28266.58	62.10		4.48		4.18	
18	67.03	62.40		4.63		4.32	
19	67.50	62.71		4.79		4.49	
20	68.02	63.01		5.01		4.61	
21	68.66	63.41		5.25		4.91	
22	69.17	63.75		5.42		5.02	
23	69.72	64.15		5.57		5.16	
24	-	64.56		-		-	
25	28271.26	64.96	—	6.30	—	5.92	—
26	71.82	65.34	—	6.48	—	6.09	—

TABLE II (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F^e	Δ_1F^f	Δ_1F^e	Δ_1F^f
27	28272.46	28266.73		6.73		6.33	
28	73.04	66.13		6.91	6.99	6.46	6.54
29	73.60	66.58	28259.59	7.02	7.08	6.57	6.63
30	74.29	67.03	59.95	7.26	7.30	6.79	6.82
31	74.98	67.50	60.20	7.48	7.57	6.96	7.05
32	-	68.02	60.45	-	7.84	-	7.31
33	-	68.55	60.71	-	8.08	-	7.58
34	-	69.05	60.97	-	8.35	-	7.82
35	28278.38	69.58	61.23	8.60	8.65	8.25	8.10
36	79.11	70.13	61.48	8.98	8.95	8.41	8.38
37	79.78	70.70	61.75	9.08	9.16	8.52	8.60
38	80.54	71.26	62.10	9.28	9.41	8.72	8.85
39	81.30	71.82	62.41	9.48	9.45	8.84	8.81
40	82.16	72.46	63.01	9.70	9.63	9.12	9.05
41	82.92	73.04	63.41	9.88	9.85	9.32	9.29
42	83.72	73.60	63.75	10.12	10.14	9.43	9.35
43	84.52	74.29	64.15	10.23	10.32	9.54	9.63
44	85.36	74.98	64.66	10.38	10.25	9.77	9.64
45	86.23	75.59	65.34	10.64	10.58	9.92	9.86

TABLE II (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F'	Δ_1F'	Δ_1F''	Δ_1F''
46	28287.28	28276.31	28265.73	10.97	10.89	10.26	10.18
47	88.32	77.02	66.13	11.30	11.12	10.52	10.44
48	89.20	77.70	66.58	11.50	11.35	10.82	10.67
49	90.18	78.38	67.03	11.80	-	11.07	-
50	91.11	79.11	-	12.00	12.12	11.33	11.45
51	92.00	79.78	28267.66	12.22	12.12	11.46	11.63
52	92.99	80.58	68.15	12.45	12.53	11.69	11.77
53	94.00	81.30	68.77	12.70	12.58	11.84	11.72
54	95.00	82.16	69.58	12.84	12.79	12.08	12.03
55	96.02	82.92	70.13	13.10	13.02	12.30	12.22
56	-	83.72	70.70	-	13.26	-	12.46
57		84.52	71.26		13.54		12.70
58		85.36	71.82		13.77		12.90
59		86.23	72.46		14.00		13.19
60		87.04	73.04		14.32		13.44
61		87.92	73.60		14.51		13.63
62		88.80	74.29		14.72		13.82
63		89.70	74.98		15.13		14.11
64		90.72	75.59		-		-

TABLE III. Vacuum Wavenumbers, Rotational Assignments and Combination Differences for the (1, 0) band of $In^{115}Cl^{35}$ Molecule.

J	R(J)	Q(J)	P(J)	$\frac{R(J)-Q(J)}{\Delta_1 F'}$	$\frac{Q(J+1)-P(J+1)}{\Delta_1 F'}$	$\frac{R(J)-Q(J+1)}{\Delta_1 F''}$	$\frac{Q(J)-P(J+1)}{\Delta_1 F''}$
18	28915.02	28910.32		4.70		4.25	
19	-	10.77		-		-	
20	28916.44	11.21		5.23		4.84	
21	16.86	11.60		5.26		4.92	
22	17.32	11.94		5.38		5.02	
23	-	12.30		-		-	
24	28918.72	12.67		6.05		5.71	
25	19.19	13.01		6.18		5.74	
26	-	13.45		-		-	
27	28920.55	13.85		6.70		6.35	
28	21.05	14.20		6.85		6.45	
29	-	14.60		-		-	
30	28922.13	15.02		7.11		6.60	
31	-	15.53		-		-	
32	-	16.04		-		-	

TABLE III (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F'	Δ_1F'	Δ_1F''	Δ_1F''
33	28924.48	28916.44		8.04	7.62	7.62	
34	25.02	16.86		8.16		7.70	
35	25.61	17.32		8.29		7.83	
36	26.19	17.78		8.41		7.97	
37	27.00	18.22		8.78		8.28	
38	-	18.72		-		-	
39	28928.48	19.19		9.29	9.31	8.85	8.87
40	29.25	19.63	28910.32	9.62	-	9.18	-
41	29.98	20.07	-	9.91	9.78	9.43	9.30
42	30.62	20.55	28910.77	10.07	-	9.57	-
43	31.35	21.05	-	10.30	10.35	9.79	9.84
44	32.07	21.36	28911.21	10.51	10.53	9.94	9.96
45	32.80	22.13	11.60	10.67	10.77	10.09	10.19
46	33.53	22.71	11.94	10.82	11.00	10.23	10.41
47	34.26	23.30	12.30	10.96	-	10.39	-
48	-	23.87	-	-	11.03	-	10.42
49	28935.73	24.48	28913.45	11.25	11.17	10.71	10.63
50	36.69	25.02	13.85	11.67	-	11.08	-

TABLE III (Continued)

J	R(J)	Q(J)	P(J)	Δ_1F'	Δ_1F'	Δ_1F''	Δ_1F''
51	-	28923.61	-	-	-	-	-
52	-	26.19	-	-	12.21	-	11.99
53	28939.41	26.31	28914.60	12.60	12.54	11.85	11.79
54	40.54	27.56	15.02	12.98	12.95	12.06	12.03
55	41.50	28.48	15.53	13.02	-	12.25	-
56	42.40	29.25	-	13.15	13.12	12.42	12.39
57	43.46	29.98	28916.86	13.48	13.30	12.84	12.66
58	44.30	30.62	17.32	13.68	13.57	12.95	12.84
59	45.19	31.35	17.78	13.84	13.85	13.12	13.12
60	46.24	32.07	18.22	14.17	14.08	13.44	13.35
61	-	32.80	18.72	-	14.34	-	13.61
62		33.53	19.19		14.63		13.90
63		34.26	19.63		14.93		14.19
64		35.00	20.07		15.18		14.45
65		35.73	20.55		-		-
66		36.50	-				
67		37.32					
68		38.04					

system, one due $^3\pi_0 - {}^1\Sigma$ and the other due to $^3\pi_1 - {}^1\Sigma$ transitions have been observed for these molecules. The $^3\pi_0 - {}^1\Sigma$ band system lies at a lower frequency as compared to the transition $^3\pi_1 - {}^1\Sigma$ showing that $^3\pi_0$ component should be the first excited state.

For Indium chloride the A-X system lying in the region 3470 Å - 3650 Å has already been assigned by Youngner and Winans[7] as appearing from the transition $^3\pi_0^+ - {}^1\Sigma^+$, having a two branch structure one P and R.

The present system shows the presence of single P, Q and R branches, so there is a great likelyhood for this system to be due to $^3\pi_1 - {}^1\Sigma$ transition. In order to verify this, an attempt is being made to correlate this excited state with that obtained from the united and separated atom models.

The ground state electronic configurations for the two atoms are:

$$In \text{ — } (KL\ldots 4spd)\ 5s^2\ 5p^1$$

$$Cl \text{ — } (KL)\ 3s^2\ 3p^5$$

Following Mulliken's notation[11] the lowest electronic configuration of the InCl molecule can be written

as

$$(KKLLM\text{spd})(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2 - {}^1\Sigma^+$$

This configuration has been said to represent the ground state of the various monohalides of Aluminium and thallium (Mioscher[5]).

The probable electronic terms may also be arrived at from the approach of the separated atoms. The ground state of the molecule is expected to dissociate into In ($^2P_{\frac{1}{2}}$) and Cl ($^2P_{3/2}$) which represent respectively the ground states of the In and Cl atoms. The electronic terms that can be derived from In (^2P) + Cl (^2P) atoms are singlet and triplet $\Sigma^+(2)$, Σ^-, $\Pi(2)$ and Δ states (Herzberg[9], page 318). The approach of the united atom will help in determining the most probable one out of these twelve terms. The electronic terms of the InCl molecule are expected to be quite similar to those of the AlCl molecule since Al belongs to the same group of the periodic table as In. Aluminium atom has got thirteen electrons with the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ and chlorine atom has seventeen electrons with the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. The molecule AlCl can be supposed to have been formed by splitting the united atom zinc which has thirty electrons. The electronic configuration

of Zn is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$ (^1S_o). The molecular state that results by splitting the zinc atom in its low lying ^1S_o state is $^1\Sigma_o^+$. Therefore a comparison of the results derived from the approach of the united and separated atoms shows that $^1\Sigma_o^+$ is the lowest of all the electronic states of the AlCl molecule and therefore also of the InCl molecule.

The configuration for the first excited state may be given as

$$(KKLLMMspd)(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)(v\pi) \quad \ldots\ldots\ldots(2)$$

This will give rise to $^1\pi$ and $^3\pi$ states. Mieschor[10] has suggested that $^3\pi$ state will be the first excited state in case of all the mono-chlorides, bromides and iodides of this group of atoms.

From the united atom approach the excited state configuration of zinc is (SPD) $4s^1\ 4p^1$ which gives rise to ^1P and ^3P states. The electronic terms of the molecule that result by splitting the zinc atom in its excited state are $^1\Sigma^+$, $^3\Sigma^+$, $^1\pi$ and $^3\pi$.

The $^1\Sigma^+$ state has already been correlated to be

the ground state. Out of the remaining eleven states derived from the separated atom model $^3\Delta$ should be the lowest and may be considered as the first excited state. The united atom approach does not give any Δ state but only Σ and Π states ruling out the possibility of $^3\Delta$ state. The next low lying state is $^3\Pi$ which can be correlated with the $^3\Pi$ state obtained from the united atom approach to be the first excited state.

Thus the united and separated atom approach alongwith the electronic configuration show that $^3\Pi$ should be most likely the first excited state of the AlCl molecule and therefore also of the InCl molecule.

The electronic configuration for the present band system may be given as

$$(x\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)(v\pi) \quad {}^3\Pi_1$$

$$\longrightarrow (x\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2 \quad {}^1\Sigma_0^+ .$$

The character of the $(x\sigma)$ and $(v\pi)$ orbitals is almost the same as there is a little difference between the vibrational frequencies of the ground and excited states of the B-X system of the InCl molecule.

REFERENCES

1. Grotrian, W. — Z.Physik 12, 229 (1923).
2. Waring, R.K. — Phys.Rev., 22, 441 (1928).
3. Winans,J.G., Davis, F. and Leitalo, V. — Phys.Rev., 57, 1079 (1940).
4. Barratt,S. and Bonar, A.R. — Phil.Mag., 2, 1519 (1930).
5. Mieschor, E. and Wehrli, M. — Helv.Phys.Acta, 7, 298 (1934).
6. Frosch,H.M. and Winans, J.G. — Phys.Rev., 72, 481 (1947).
7. Youngner, P. and Winans, J.G. — J.Mol.Spect., 4, 23 (1960).
8. Barrett,A.H. and Mandel, M. — Phys.Rev., 99, 666 (1955).
9. Herzberg, G. — Spectra of Diatomic Molecules (Van Nostrand, New York), 1950.
10. Mieschor, E. — Helv.Phys.Acta, 8, 279 (1935).
11. Mulliken, R.S. — Rev.Mod.Phys., 4, 1 (1932).

ABSTRACT

The thesis entitled "THE ELECTRONIC STUDIES OF LEAD BROMIDE, BISMUTH BROMIDE AND INDIUM CHLORIDE MOLECULES" submitted to the Aligarh Muslim University, Aligarh, India, in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Physics, describes in three chapters the rotational analyses of the A-X system of the PbBr and the BiBr molecules and the B-X system of the InCl molecule. The spectra of these halides have been excited mostly with the help of a 2450 Mc/sec microwave oscillator as well as with an eight kilowatt transformer.

The emission spectrum of the visible band system of the PbBr molecule in the region 4600 Å - 6100 Å has been obtained. About 110 bands have been observed in the present experiment of which only 52 were recorded by earlier workers. The vibrational constants obtained are the same as those obtained by Morgan from absorption experiments.

The rotational structure of some of the bands of this system has been recorded in the second order of a 35 ft concave grating spectrograph at a dispersion of 0.32 Å/mm and the analysis of four bands (3, 2), (2, 2), (4, 2) and (4, 1) has been done. In all four branches have been observed for each of the bands and they have

been explained as the P and R branches due to $Pb^{79}Br$ and $Pb^{81}Br$. The molecular constants obtained are:

	$Pb^{79}Br$	$Pb^{81}Br$
B_0' cm^{-1}	0.0369	0.0378
B_0'' cm^{-1}	0.0455	0.0446
r_0' Å	2.76_8	2.76_6
r_0'' Å	2.54_6	2.54_5

$\alpha_e' = 0.00015$ cm^{-1} ; $\alpha_e'' = 0.00015$ cm^{-1}

$D_2'' = 1.0 \times 10^{-8}$ cm^{-1} ; $D_4' = 2.0 \times 10^{-8}$ cm^{-1}

The rotational structure of the visible band system (4600 Å – 6350 Å) of the BiBr molecule has been recorded in the second order of a 35 ft concave grating spectrograph at a reciprocal dispersion of 0.32 Å/mm. The structure due to two isotopes of bromine has been resolved. A rotational analysis of (7, 0), (8, 0), (9, 0), (10, 1), (1, 4), (0, 6) and (0, 7) bands of this system has been carried out leading to the determination of the following rotational constants:

	$Bi^{79}Br$	$Bi^{81}Br$
B_0' cm^{-1}	0.0064_2	0.0358_2
B_0'' cm^{-1}	0.0436_7	0.0428_7
r_e' Å	2.84_2	2.84
r_0'' Å	2.59_6	2.59_6

$\alpha_e' = 0.00025$ cm^{-1}; $\alpha_e'' = 0.00015$ cm^{-1}; $D_0'' = 5.0 \pm 4.0 \times 10^{-8}$ cm^{-1}.

As the structure shows the presence of only P and R branches, the system appears to be similar to the visible band system of the BiCl molecule and a Hund's case (C) type $^3\Pi(0^+) - {}^3\Sigma^-(0^+)$ transition has been suggested.

The emission spectrum of the InCl molecule has been excited and the bands lying in the near ultraviolet region (3400 Å – 3650 Å) have been photographed in the second order of a 35 ft concave grating spectrograph. The rotational lines of the (0, 0), (0, 1) and (1, 0) bands of the B–X system have been identified and their wave-numbers determined. The analyses of the bands have been carried out leading to the determination of the following constants for $In^{115}Cl^{35}$ molecule:

$B_e' = 0.1198\ cm^{-1}$	$B_e'' = 0.1093\ cm^{-1}$
$r_e' = 2.330$ Å	$r_e'' = 2.399$ Å
$\alpha_e' = 8 \times 10^{-4}\ cm^{-1}$	$\alpha_e'' = 5 \times 10^{-4}\ cm^{-1}$
$D_e' = 3.0 \times 10^{-8}\ cm^{-1}$	$D_e'' = 2.4 \times 10^{-8}\ cm^{-1}$.

The value of the ground state internuclear distance agrees with that obtained by Youngner and Winans from the absorption experiment. The probable electronic configurations for the states involved in the transition of this band system have been arrived at from a correlation of the united and separated atom model approach.